[*Frontispiece*

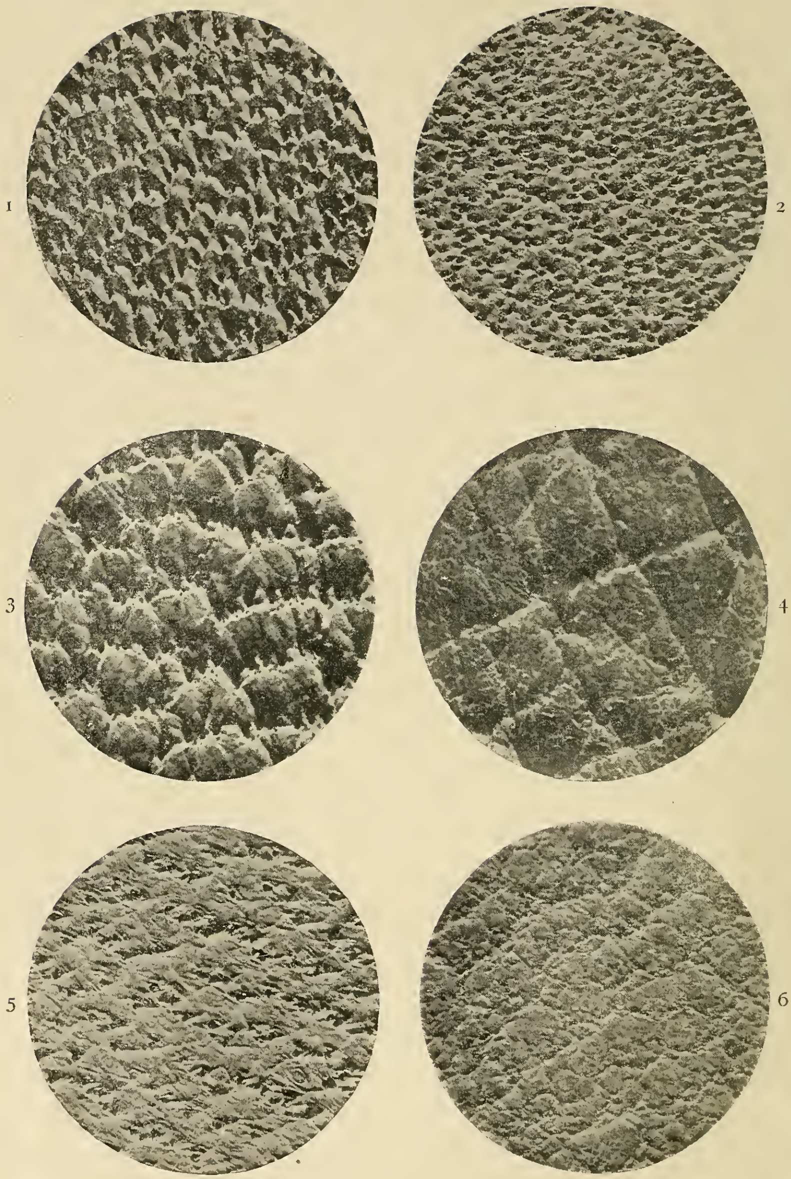

Photo-micrographs of Grain of various Skins (*A. Seymour-Jones*).

1. Cow-hide; 2. Calf-skin; 3. East India Goat; 4. Pig-skin;
5. East India Sheep; 6. Welsh Sheep.

THE PRINCIPLES OF
LEATHER MANUFACTURE

BY

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THE MEMORY OF

THE LATE PROFESSOR F. L. KNAPP

GEHEIMEN HOFRATH, DR. PHIL. AND DR. ING.

THE PIONEER OF SCIENTIFIC RESEARCH

IN LEATHER MANUFACTURE

PREFACE TO SECOND EDITION

In the eighteen years which have elapsed since the publication of the first edition, not only have great advances been made in the chemical knowledge on which the manufacture is based, but new points of view have been gained, involving an acquaintance with physical and colloidal chemistry which is not yet universal among leather-trade chemists, and I have felt compelled to enter into elementary details of these branches of science which, no doubt, in a few years will be among the commonplaces of chemical knowledge. I must therefore repeat the apology of the first preface, that to some of my readers much will necessarily seem too elementary, while to others it may prove too difficult, though I have endeavoured, as much as possible, to confine mathematical treatment to notes and appendices. It may be pointed out, however, that the advance of the future will necessarily tend to exact and mathematical methods, and that many theories which seem plausible enough when stated qualitatively and in general terms will break down when submitted to the rigorous examination of mathematics.

The third volume on the *Methods of Leather Manufacture*, which was suggested in the former preface, yet remains to be written, but advancing age renders such a work impossible to the present writer, and its execution must be left to some of the young and well-trained chemists who are now devoting themselves to the trade.

It is my pleasant duty to acknowledge much indebtedness to Mr F. C. Thompson, my Assistant in the Procter International Research Laboratory, not only for re-writing the chapters on the Chemistry of Hide and on that of the Tannins, with which he has made himself specially familiar, but for much general assistance both in the preparation of the work and in the reading of proofs; to Mr W. R. Atkin for his permission to insert the paper on hydrion measurement which appears in Appendix D, and also for help in proof-reading; and to the various gentlemen who have given information and allowed me to use their blocks and drawings in illustration; and especially to Mr A. Seymour-Jones, Professor McCandlish, Mr J. T. Wood, and Mr M. C. Lamb.

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PREFACE TO FIRST EDITION

The origin of the present work was an attempt to prepare a second edition of the little *Text-book of Tanning* which the Author published in 1885, and which has been long out of print. Though persevered in for years, the work was never brought to completion, partly owing to the constant pressure of other duties, but still more to the rapid advances which have been made in our knowledge of the subject, and in the scientific thought which has been devoted to it. For his share in the initiation of this work much credit is due to Wilhelm Eitner, Director of the Imperial Royal Research Institute for Leather Industries in Vienna, but the advance he began has been energetically carried forward not only in Vienna, but in the Tanning Schools and Research Institutes of Freiberg, Leeds, London, Liége, Copenhagen, Berlin, and elsewhere, and to a less extent in private laboratories.

Under the pressure of this rapid growth, as it was impossible to complete the work as a whole, the Author published an instalment dealing with the purely chemical side of the subject in 1898, under the title of the *Leather Industries Laboratory Book*; which has been translated into German, French, and Italian, and of which the English edition is rapidly approaching exhaustion.

The present work, which should by right have preceded the Laboratory Book (and which frequently refers to it as "L.I.L.B."), attempts to deal with the general scientific principles of the industry, without describing in detail its practical methods (though incidentally many practical points are discussed). To complete the subject a third volume ought to be written, giving working details of the various methods of manufacture; but apart from the difficulty of the subject, and the weariness of "making many books," the methods of trade are so fluctuating, and dependent on temporary conditions, that they have not the same permanent value as the record of scientific advance.

As the present volume is intended to appeal both to the chemist and to the practical tanner, it must to a certain extent fail in both, since many matters are included which are already familiar to the former, and, it is to be feared, some which may prove difficult to the latter. For these and other imperfections the Author claims the indulgence of his Readers.

The Author must here acknowledge his indebtedness to Dr Tom Guthrie and to Mr A. B. Searle for assistance in writing several of the chapters ; to Dr A. Turnbull and Mr F. A. Blockey for much help in reading proofs and preparing the MS. for the press ; and to the many gentlemen who have furnished or allowed him to use their blocks and drawings in illustration.

The Yorkshire College,
Leeds.

CONTENTS

THE PRINCIPLES OF LEATHER MANUFACTURE

CHAPTER I

INTRODUCTORY AND HISTORICAL

THE origin of leather manufacture dates far back in the prehistoric ages, and was probably one of the earliest arts practised by mankind. The relics which have come down to us from palæolithic times, and the experience of the modern explorer, alike tell us that agriculture is a later and a higher stage of development than the life of the hunter ; and since, in the colder regions, clothing of some kind must always have been a necessity, we may conclude that it was first furnished by the skins of animals.[1]

While wet skins putrefy and decay, dry ones are hard and horny ; and nothing could be more natural to the hunter than to try to remedy this by rubbing the drying skin with the fat of the animal, of which he must have noticed the softening effect on his own skin. By this means a soft and durable leather may be produced, and this process of rubbing and kneading with greasy and albuminous matters, such as fat, brains, milk, butter, and egg-yolks, is in use to this day, alike by the Tartars on Asiatic steppes and the Indians on American prairies ; and not only so, but we ourselves still use the same principle in the dressing of our finest furs, and in the manufacture of chamois, and many sorts of lace- and belt-leathers.

Such a process is described in the *Iliad* (xvii. 389–393) in the account of the struggle over the body of Patroclus :

> " As when a man
> A huge ox-hide drunken with slippery lard
> Gives to be stretched, his servants all around
> Disposed, just intervals between, the task
> Ply strenuous, and while many straining hard
> Extend it equal on all sides, it sweats
> The moisture out and drinks the unction in."

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[1] See also Gen. iii. 21.

It must also have been early noticed that wood smoke, which in those days was inseparable from the use of fire, had an antiseptic and preservative effect on skins which were dried in it, and smoked leathers are still made in America, both by the Indians and by more civilised leather manufacturers. To this method the Psalmist refers [1] when he says, " I am become like a bottle in the smoke " ; and such bottles, made of the entire skin of the goat, are still familiar to travellers in the East.

The use of vegetable tanning materials, though prehistoric, is probably less ancient than the methods I have described, and may possibly have been discovered in early attempts at dyeing ; an art which perhaps had its origin even before the use of clothing ! The tannins are very widely distributed in the vegetable kingdom, and most barks, and many fruits, are capable of making leather.

The employment of alum and salt in tanning was probably of still later introduction, and must have originated in countries where alum is found as a natural product. The art was lost or unknown in Europe till introduced into Spain by the Moors.

Leather manufacture reached considerable perfection in ancient Egypt. A granite carving, probably at least 4000 years old, is preserved in the Berlin Museum, in which leather-dressers are represented. One is taking a tiger-skin from a tub or pit, a second is employed at another tub, while a third is working a skin upon a table. Embossed and gilt leather straps have been found on a mummy of the ninth century B.C., and an Egyptian boat-cover of embossed goat leather, as well as shoes of dyed and painted morocco, are still in comparatively good preservation. The art is of very early date in China, and was well understood by the Greeks and Romans. In the Grosvenor Museum at Chester is the sole of a Roman *caliga*, studded with bronze nails, which is yet pretty flexible ; and Roman shoes have been found in other parts of England in not much worse condition than those which tramps leave by the wayside. After the fall of the Roman empire many arts were lost to Europe, and it was not until the Moorish invasion of Spain that the art of dyeing and finishing the finer kinds of leather was reintroduced.

England was very backward in this manufacture up to the end of the eighteenth century, owing to the fossilising influence of much paternal legislation, and of certain excise-duties, which were only repealed in 1830. Since this time the art has made rapid strides, especially in the use of labour-saving machinery, and England may at the present moment be considered fairly abreast of any other country as a whole ; though in some special

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[1] Ps. cxix. 83.

manufactures we are surpassed by the Continent and by America. In making comparisons of this kind, it must, however, be remembered that, especially in sole-leather tannage, the most rapid progress has been made during the last few years in those countries which were more backward, and that therefore our superiority is much less pronounced than formerly, and in a few years may cease to exist unless marked improvements are introduced in the methods of production. The past twenty years have, however, been marked by very considerable advance, and the application of science to the manufacture has been very noticeable.

In the sketch of the development of leather manufacture which has just been given, it has been implied that its object is to convert the putrescible animal skin into a material which is permanent and not readily subject to decay, while retaining sufficient softness or flexibility for the purposes for which it is intended. As these range from boot-soles to kid-gloves, there are wide divergences, not only in the processes employed, but also in the materials used and in the principles of their application. The most important method of producing leather is still by the use of vegetable tanning materials, and this is perhaps the only one which is really entitled to be called " tanning," though the distinction is not very strictly adhered to. It includes the whole range—from sole leather, through strap, harness and dressing leather, to calf and goat skins, and the various sumach tannages which yield morocco and its imitations. All of these products but the first and the last undergo, after tanning, the further processes of " currying," of which the most important operation consists in " stuffing " with oily and fatty matters, both to increase the flexibility and to confer a certain amount of resistance to water. Sumach-tanned skins are not strictly " curried," but usually receive a certain amount of oil in the process of " finishing."

With the vegetable tans we may include Stiasny's synthetic organic tannins, " Neradol D " and others, produced by condensation of formaldehyde with phenolsulphonic acids (see also p. 343), which produce a perfectly white leather when used alone, and can be combined with other tans to give a paler leather and to quicken tannage.

Next in importance to the vegetable tannages are those produced by salts of chromium and aluminium, including all the various " chrome " leathers, and the " tawed " or " white " leathers, used for whip-lashes, belt-laces, and aprons, as well as for calf- and glove-kid.

Connecting links between these and the vegetable tannages are found in "green leather," "Dongola" and other combination tannages in which alum and salt are employed in conjunction with vegetable materials; and in "semi-chrome" and other leathers in which chrome salts are used instead of those of alumina. Formaldehyde also is becoming of importance as an adjunct to other tannages.

In the production of calf- and glove-kid, in addition to alum and salt, albuminous and fatty matters, such as egg-yolk, olive oil, and the gluten of flour, play a considerable part, and are thus linked both to the primitive methods in use by the Indians and Kalmucks, and to those by which "crown" and "Helvetia" leather, and many other forms of belt- and lace-leathers, are now produced by treatment with fats and albumens.

From these again the step is a short one to the "chamois" and "buff" leathers, and the German "*fettgar*" leathers, in which oils and fats only are used.

In an attempt to view all these complex processes from the scientific standpoint, the reader should constantly realise that the present methods of leather manufacture are the results of tens of centuries of experience, and of innumerable forgotten failures, and must not therefore expect that they can be easily superseded. Science must follow before it can lead, and its first duty is to try to understand the reasons and principles of our present practice, for we can only build the new on the foundation of what has been already learned. Another fact, which is scarcely understood by the practical man in his demands on science, is that in leather manufacture every question which is raised seems to rest on the most recondite problems of chemistry and physics; the chemistry of some of the most complex of organic compounds, and the physics of solution, of osmose, and of the structure of colloid bodies—problems which are yet far from completely conquered by the highest science of the day. Many of these problems are, however, rapidly yielding to investigation, and we may anticipate that science, and especially chemistry, will play a constantly increasing part in the technology of leather manufacture.

It may seem bold to attempt the scientific treatment of such a subject at all; and, indeed, it must be admitted that our knowledge is still inadequate for its complete accomplishment, but much has been done in the last twenty years, and this can at least be summarised and arranged in an available form. The subject falls naturally into two sections, in the first of which the processes of manufacture would only be described in general terms, and with sufficient fulness to enable the reader to understand the scientific considerations on which they are based, and the methods of investigation which can be applied to them; while in the second an effort should be made to give working details of the various processes sufficient to enable those with a general knowledge of the trade to experiment successfully in its various branches. It was at first intended that these two sections should be published in one book as a second edition to the Author's *Text-book of Tanning*, but owing to the long delay in its publication, it was decided to publish the first section under the present title *The Principles of Leather Manufacture*, leaving the latter section *Processes of Leather Manufacture* to a later date. It is improbable that, for the present writer, this date will ever arrive, but the work has been to some extent done by others, and especially by Bennett in his *Manufacture of Leather* (Constable & Co., London, 1909); while the more strictly chemical portion has already appeared in the *Leather Industries Laboratory Book*, frequently referred to in the following pages under the abbreviation "L.I.L.B.," and in the *Leather Chemists' Pocket Book*, "L.C.P.B." Where quantities and details are given, they must not be taken as recipes to be blindly followed; or even, in every case, as the best-known methods; but rather as mere guides to experiment, which must be modified to suit varying conditions and requirements. It is the special virtue of the scientific, as opposed to the merely traditional, way of looking at such questions, that knowing the cause and effect of each part of the process, it can so adjust them as to get over difficulties, and to suit novel conditions; although much time may be wasted in useless experiments, if approximate and practical quantities and methods are not known. It is needless to add that many methods are jealously preserved as trade secrets, and full details are frequently unattainable, though this is less the case than formerly.

After what has just been said, it may be well to emphasise the great importance of practical knowledge and experience to the leather manufacturer. Even in trades which have reached the highest scientific development, such, for instance, as the manufacture of the coal-tar colours, the small experiments of the laboratory are not transformed into manufacturing operations without experience and sometimes even failure; and this must still more often be the case in a trade like that of leather-making, where our knowledge of the actual changes involved is so incomplete. On the other hand, the cost of experiments on a manufacturing scale is usually so heavy that the least scientific must admit the advantage of learning all which the laboratory can teach before venturing further; while even our present imperfect knowledge of the chemical changes involved will often warn us off hopeless experiments, and give us hints of the directions in which success may be attained. A knowledge of chemistry will certainly prove at least as important to the future of our trade as that of mechanics has been in the past.

CHAPTER II

INTRODUCTORY SKETCH OF LEATHER MANUFACTURE

THE object of tanning has been stated to be the rendering of animal skin imputrescible and pliable, but as we now rarely require leather with the hair on, preliminary processes are needed to remove it and to fit the skin for tanning; and the nature of these processes has great influence on the subsequent character of the leather produced.

The first step is usually a washing of the skin to remove blood and dirt; while, where it has been salted or dried, a more thorough soaking is needed to remove the salt, and to restore the skin to its original soft and permeable condition.

The hair is then loosened by softening and partial solution of the epidermis structures (see p. 49) in which it is rooted. This is most generally accomplished by soaking for some days in milk of lime, which is usually assisted by the addition of alkaline sulphides. When the latter are used in concentrated solution, the hair itself, as well as the epidermis tissues, is softened and destroyed in the course of a few hours. The lime not only serves to loosen the hair, but swells and splits up the fibre-bundles of which the hide tissue is composed, and so fits it to receive the tannage (*cp.* p. 58); and the process is always complicated and assisted by bacterial activity.

For some purposes a regulated putrefactive process is indeed substituted for the liming; the hides or skins being hung in a moist and warm chamber (see p. 166), when the soft mucous layer which forms the inner part of the epidermis is disintegrated, partly by direct putrefaction, partly by the action of the ammonia evolved, so that the hair can be scraped off. In this case the hide-fibre is not swollen, and the necessary swelling has to be obtained by subsequent processes.

In whatever way the hair has been loosened, it is either scraped off with a blunt and somewhat curved two-handled knife on a sloping rounded "beam" of wood or metal, or removed by a suitable machine, this operation being termed "unhairing" (see p. 191).

This is generally followed by "fleshing," which is performed on the same beam with a somewhat similar knife, which, however, is two-edged and sharp. In this operation, portions of flesh, and the fat and loose tissue which underlie the true skin (see p. 193), are removed by scraping and cutting. Machines for fleshing are also largely in use (see p. 196).

For sole leather, the hide, after some washing in soft water or treatment with weak acid solutions to cleanse from lime, is then ready for the actual tanning process ; but for the softer leathers more thorough treatment is needed to remove the lime, and to still further soften the skin by solution and removal of a portion of the cementing substance and of the elastin fibres.

This treatment was generally of a fermentative or putrefactive nature, and the most common form was that known as " bating," which consists in steeping in a fermenting infusion of pigeon- or hen-dung. The theory of its action is not yet thoroughly understood, but the effect is largely due to the unorganised hydrolysing ferments produced by the *bacteria* present ; while at the same time the lime is neutralised and removed by the weak organic acids and salts of ammonia which are produced, and the fibres, which had been plump and swollen with lime, becomes extremely relaxed and flaccid. This process and that of puering have been largely superseded by the direct use of trypstic ferments derived from the pancreas of animals in conjunction with ammonium chloride to remove the lime (Chap. XIV.).

In the lightest leathers, such as kid- and lamb-skins for gloves, and goat and sheep for moroccos and the like, dog-dung is substituted for that of fowls, and the process is then called " puering " (see p. 230).

These processes are often followed by " drenching," which sometimes indeed takes their place, the skins being soaked in a fermenting bran infusion. In this, the small quantities of acetic and lactic acid formed by fermentation are the active agents, neutralising and dissolving the lime, and cleansing and slightly plumping the pelt (see p. 214).

In recent times these unpleasant processes have been largely supplemented, and in some cases superseded, by purely chemical means, which are safer and more economical.

The tanning process which follows consists in soaking the pelt in infusions of various vegetable products containing bodies of the class known as " tannins," which have the power of combining with skin-fibre and converting it into leather.

If at first strong infusions were used, they would act too violently on the surface of the skin, hardening and contracting it so that the subsequent tannage of the interior would be impeded, and the " grain " or outer surface would be " drawn " and wrinkled. This is avoided by the use at first of very weak infusions which have already been partially exhausted on goods in a more advanced stage. In the later part of the process much stronger solutions are employed, and the hides are frequently " dusted " in them with ground tanning material.

In the case of sole leather, these processes may require from two to twelve months for completion ; after which the leather is dried, smoothed, and compressed by mechanical means, and is then ready for use. The time of tannage is now often shortened by " drumming " and other processes of agitation.

Dressing-leathers, ranging from calf-skins to harness-hides, receive a much shorter tannage, and a subsequent treatment with fats and oils, which, together with mechanical manipulations, constitute " currying." The thin film of grease distributed over the surface of the fibres renders them supple, and to some extent waterproof.

The lighter fancy leathers, such as morocco, are dyed, and undergo many complex processes to fit them for their required purposes and improve their appearance.

Many skins, such as calf, glove, and glacé kid, are not tanned, but " tawed " by a solution of alum and salt, which is often supplemented with mixtures of flour and egg-yolk to fill and soften the leather.

Salts of chromium are now largely employed in place of alum and salt, and produce an equally soft, but more permanent and enduring, leather, and the process is also applied to the production of the firmer leathers required for soles and beltings.

Lastly, wash-leather, or so-called " chamois," and buff-leather are produced by fulling the prepared pelt with fish or whale oil, which converts the skin into leather by subsequent oxidation, during which aldehydes are evolved.

CHAPTER III

THE LIVING CELL

The larger part of the materials employed in leather manufacture are organic in their origin, and the skin itself is an organised structure, while the life-processes of putrefaction and fermentation play a large part in the tannery. Some knowledge, therefore, of biological structures and processes is necessary to a full understanding of much which follows, and a few words are not out of place with regard to the foundations of life itself.

The bricks of which all living structures are built are the living " cells " and their products, and these first elements differ little, if at all, whether the life is animal or vegetable, the distinction being produced rather by the way in which they are put together than by differences in the cells themselves. This is so much the case that it is often difficult to decide in which of the two classes to place the simplest organisms, since many of these forms are capable of active movement, and their modes of nutrition and reproduction are common to both kingdoms.

In its simplest form, the cell, whether animal or vegetable, is strictly speaking not a cell at all, but consists merely of a minute mass of living jelly or protoplasm. Such is the amœba found in water and damp soil, such are the lymph-cells and white blood-corpuscles of our bodies, and such also some stages at least of the lowest forms of fungi, like the *Æthalium septicum*, which is sometimes found on old tan-heaps as a crawling mass of yellow slime. If a drop of saliva be examined with the microscope under a cover-glass, with one-sixth objective and small opening of diaphragm,[1] a few scattered semi-transparent objects will be found, of the apparent size of a lentil or small pea, and of rounded form. These are lymph-corpuscles (fig. 1). Their contents are full of small granules, and if they be observed quickly, or if the slide be kept at about the warmth of the body, it will be noticed that these are in constant streaming motion. If the warmth can be kept constant, which is difficult without special apparatus, and the cells can be observed from time to time, it may be seen that they lose their circular form, and put out pro-

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[1] For details of microscopic manipulation in this and the following chapter see *L.I.L.B.*, pp. 411 *et seq.*, and *L.C.P.B.*, pp. 199 *et seq.*

tuberances (pseudopodia, "false feet"), one of which will gradually increase in bulk, till it absorbs the whole cell, which thus crawls about. It will now readily be understood how these cells wander through all the tissues of the body, passing through the smallest pores like the fairy who put her finger through a keyhole and grew on the other side till she was all through! This independent vitality, in a warm and suitable nutrient liquid, may continue quite indefinitely.

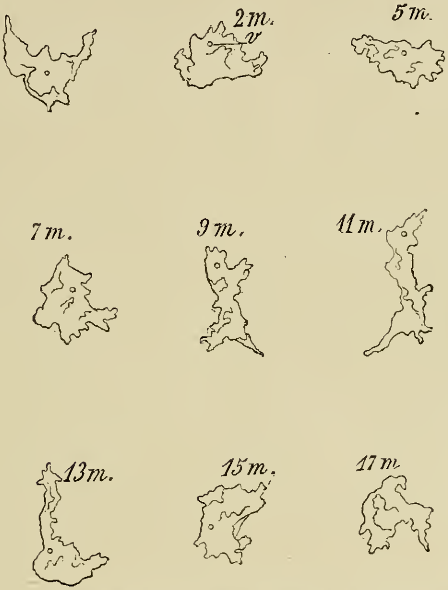

FIG. 1.—Lymph-corpuscle of frog, showing gradual change of form. (Ranvier.)

It is possible that by close attention, a rounded or elongated body, somewhat like an oil-globule, may be seen within the cell, though it is generally more obvious when the latter has been killed and stained with a weak solution of iodine. This is the nucleus, and within it is a still smaller speck called the nucleolus, which bears an important, and as yet little understood, part in the life-history of the cell. After a period it undergoes certain complicated changes in its internal structure, and divides into two, the nucleus elongates, and also divides, each half carrying with it a portion of the living protoplasmic jelly, and thus forming two complete and independent cells. This is the life-history, not only of the lymph-cell, but, with more or less modification, of every living cell or tissue.

These cells, like all living things, feed on the nutriment which surrounds them, and even enclose small particles of solid food, which are gradually dissolved and disappear. In this way the white blood-corpuscles are said to feed upon and destroy the still smaller organisms which gain access to the blood, and which might otherwise cause disease, and to absorb and remove dead tissues. The matter which cells consume is not, of course, destroyed, but simply converted into other forms, some of which are useless, or even poisonous to the cells, and which, like the secretions of higher animals, are discharged into the surrounding fluids ; while others are retained, and contribute to the growth of the cell. Thus most vegetable cells secrete cellulose, or plant-tissue, which forms a wall enclosing the protoplasm, and so justifies the name of cell. If to warm water and a little sugar we add enough yeast to render it slightly milky, and examine it like the saliva, we shall have before us typical vegetable cells of the simplest form (fig. 2). There is the same granular protoplasm, and there is the nucleus, though it cannot be seen without special preparation, the rounded spaces which look like nuclei being simply filled with transparent fluid, and called vacuoles. There is, however, no motion, as in the case of amœba, for the cells are enclosed in a tough skin of cellulose, which will be evident if they are crushed by putting some folds of blotting-paper on the cover-glass and pressing it with the handle of a needle or a rounded glass rod, when the protoplasm will be forced out and

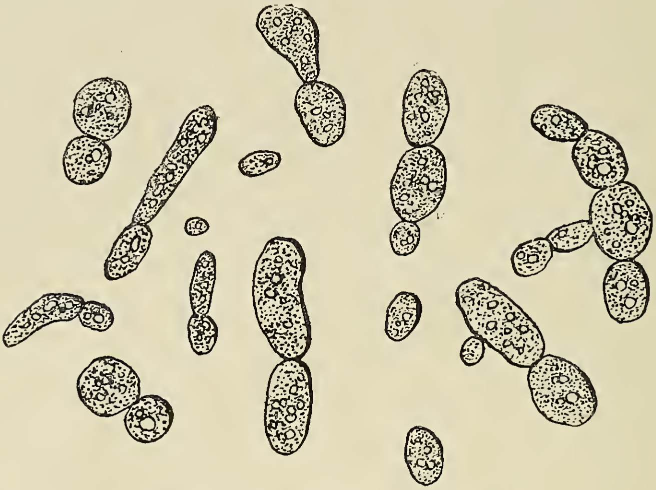

Fig. 2.—Yeast-cells, much magnified.

the skin remain like a burst bladder. This will be more obvious if the cells are previously treated with iodine or magenta, which will stain the protoplasm, but not the membrane. It is easy to observe the multiplication of the yeast-cells, which is somewhat different to that of the corpuscles. Instead of enlarging as a whole, and dividing into two equal cells, a small bud appears on the side of the parent-cell, and enlarges till it becomes itself a parent-cell with buds of its own. These do not break away at once, and hence chains and groups of attached cells are formed which are easily noticed in growing yeast if a microscope be employed. The principal nutriment of yeast is grape-sugar or glucose ; and much more of this is consumed than is needed to produce the cellulose wall and the substance of new cells ; just as in the animal, sugar, starch, and fat are consumed to give heat and energy. In the yeast, this extra sugar is split up into carbon dioxide, which escapes as gas, and to which yeast owes its power of raising bread ; and into alcohol, which in too large proportion is poisonous to the yeast itself.

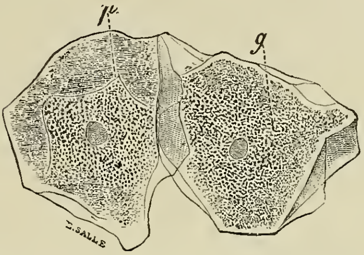

FIG. 3.—Epithelium-cells. (Ranvier.) *p*, pressure-marks ; *g*, granular protoplasm.

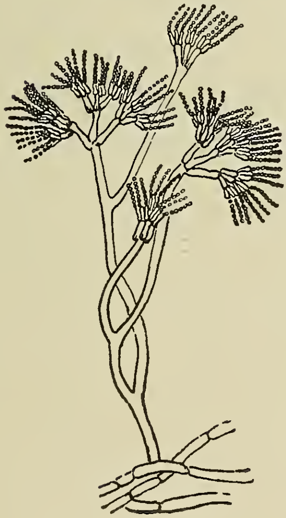

FIG. 4.—*Penicillium glaucum*, a common green mould.

In examining the saliva for lymph-cells, it is probable that some much larger objects may have been noticed of irregular polygonal outline and with a well-marked nucleus. These are cells from the lining *epithelium* of the mouth, and only differ from those of the *epidermis* of skin in their form and size (fig. 3). Note the markings caused by the pressure of overlapping cells. In these cells the wall is formed of keratin or horny tissue, which takes the place of the cellulose of the yeast.

Other simple forms of cell are those of *Saccharomyces mycoderma* or *torula*, which forms a skin on the surface of old liquors, and which much resembles a small yeast; and of the various ferments which are found in liquors, bates and drenches, which will be more fully described in the chapter following.

Many of these, such as the acetic and lactic ferments, which, like all other *bacteria*, multiply by division, do not separate, but remain connected in chains or chaplets, like a string of beads. From these, the step is not a long one to the *hyphæ* or stems of the higher moulds, which are too frequently found on leather which has been slowly dried, and which consist simply of tubular cells which elongate and divide by the formation of *septa* or cross-partitions, and thus build up a complicated plant-structure (fig. 4). As we proceed higher in the scale of plant and animal life the forms and products of the cells become more varied, and instead of one single cell, fulfilling all the functions of the plant or animal, each class of cell has its own peculiar duties and properties, while all work together for the maintenance of the complex structure of which they form a part.

CHAPTER IV

PUTREFACTION AND FERMENTATION

The chemical changes produced by the unicellular plants, such as yeasts and bacteria, to which allusion has been made in the last chapter, are known as fermentation and putrefaction, and are of such importance to the tanner, both for good and evil, that the subject must be treated in some detail. No scientific distinction exists between fermentation and putrefaction, though it is customary to restrict the latter term to those decompositions of nitrogenous animal matter which yield products of disagreeable smell and taste.

The organisms which are the cause of both fermentation and putrefaction are known by the general term of "ferments." This term has also been extended in recent years so as to include the so-called "unorganised ferments" (enzymes, zymases), which are active digestive products secreted by bacteria and other living organisms, and which are constantly increasing in both scientific and technical importance.

The organised ferments are again divided into three classes :—

1. Moulds.
2. Yeasts (Saccharomycetes).
3. Bacteria.

The members of one class are distinguished from those of another by their form, and, more especially, by the substances they produce during their life-history. All three classes are now considered to be fungi.

All enzymes possess the following three properties :—

1. They are nitrogenous bodies.
2. They are unstable, *i.e.* they are destroyed by heat, chemicals, etc.
3. A relatively small quantity of the ferment is capable of producing great changes in the substances upon which it acts, especially if the products of the change can be removed as they are formed. In these qualities they resemble the substances known as "catalysts" in chemistry, and their action must be regarded as a species of catalysis.

The general character of fermentation will be best understood by a closer study of the yeast-cell, which has already been described (p. 12), and its life-history briefly sketched. It has been shown that it is a growing plant of a very simple type, belonging to the fungi. These are devoid of the green colouring matter which enables the higher plants to utilise the energy of sunlight in assimilating the carbonic acid of the atmosphere, exhaling its oxygen, and employing its carbon for the building up of tissue; and they must therefore, like animals, have their nutriment ready formed, and capable of supplying energy by its oxidation. For yeast, as has been stated, the appropriate nourishment is glucose, or "grape-sugar." This is broken down, in the main, into the simpler compounds, alcohol and carbonic acid, while a small portion is utilised for the building up of the cell and the formation of secondary products. The main reaction is represented by the following equation:—

$$\underset{\textit{Glucose}}{C_6H_{12}O_6} = \underset{\textit{Alcohol}}{2C_2H_6O} + \underset{\textit{Carbon dioxide}}{2CO_2}$$

Yeast cannot directly ferment ordinary cane-sugar ($C_{12}H_{22}O_{11}$), but secretes a substance called invertase, which so acts on the sugar as to break it up, with absorption of one molecule of water, into two molecules of fermentable glucose (dextrose and levulose) which serve as nourishment for the yeast.[1] This invertase is a type of the series of bodies which we have spoken of as "unorganised ferments," enzymes, or zymases, differing from the organised ferments in being simply chemical products without life or power of reproduction, but capable of breaking up an unlimited quantity of the bodies on which they act, without themselves suffering change. The way in which this is done is not clearly understood, but some parallel may be found to it in the action of sulphuric acid on alcohol, of which it will convert an unlimited quantity into ether, without itself suffering any permanent change. The action of enzymes is limited to breaking down complex bodies into simpler forms, often with absorption of water, as in the case of sugar, while some of the products of living ferments are often complex, a part of their nutriment being broken down into simple products, such as carbonic acid, marsh gas, and ammonia, to supply the necessary energy to elaborate the remainder.

Very many different unorganised ferments are known to exist, as they are not only produced by yeasts and bacteria, but are

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[1] Compare O'Sullivan and Thompson, *Journ. Chem. Soc.*, 1890, p. 834; 1891, p. 46.

formed by the cells of higher plants and animals; thus the digestive principles, pepsin, trypsin, ptyalin, are of this character —ptyalin, like diastase, converting starch into sugar; and such bodies fulfil many functions both in animal and vegetable economy. In fermentation, as in disease, it is often difficult to distinguish what is due to the direct action of bacteria and what to the unorganised ferments which they produce, and the question is further complicated by the fact that in most natural fermentations more than one ferment-organism is present. Sometimes the action of the unorganised ferments may be distinguished by the fact that the addition of chloroform has little effect on their activity, while it paralyses that of the living organism. By exposure to high temperature both are destroyed, the bacteria, yeasts, and moulds being killed and the unorganised ferments coagulated like white of egg, and so rendered inoperative. Many antiseptics also destroy the activity of both organisms and enzymes; but others, like chloroform, have no action on the latter. In many cases, as in that of invertase, the actual zymase can be precipitated by alcohol from its aqueous solution, filtered off, and restored to activity by transference into water. Wood found that the enzymes so separated from a puer liquor were still active after fourteen years. Since both classes of ferments are destroyed by high temperatures, all fermentation-processes are completely and permanently arrested by exposure to sufficient heat, and subsequent preservation in vessels so closed that no new ferment-germs can gain access. A familiar instance is that of tinned meats. All fully developed bacteria are destroyed by a very short exposure to a boiling temperature, and most by 60° to 70° C., but many species produce spores which are extremely difficult to destroy. The thermophilic bacteria discovered by Globig and further investigated by Rabinowitsch[1] thrive at a temperature of 60° C. About eight species of these are known, and they take part in the heating of hay and similar fermentations where high temperatures are involved, and are therefore presumably present in spent tan.

The spores of the anthrax bacterium, the cause of the malignant pustule and of "wool-sorters' disease," are extremely resistant both to heat and to disinfectants. (*Cp.* p. 236.)

For absolute sterilisation it is therefore necessary either to boil under pressure so as to raise the temperature to, say, 110° C., or to heat repeatedly for a short time to temperatures of 80° to 100° C. at successive intervals of twenty-four hours, in order to allow the spores to develop. This process is frequently per-

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[1] *Centr. Blatt für Bakt.*, II. Abth., vol. i. p. 585.

formed for bacteriological observation in flasks or test-tubes merely stopped with a plug of sterilised cotton-wool, which has been found to filter efficiently the germs from the air which enters through it (see *L.I.L.B.*, p. 440 ; *L.C.P.B.*, pp. 209 *et seq.*).

The ferment-organisms cannot thrive and multiply unless they have proper nourishment and conditions of growth, the amount of moisture and the temperature being two of the most important of the latter. Use is made of this in the preservation of many articles of food, etc., since by ensuring that at least one of the conditions necessary for growth shall be absent, these substances are prevented from decomposing. For instance, hides are preserved by drying them ; the absence of sufficient moisture hindering the growth of any organisms in them so long as they are dry, but as soon as they become somewhat damp, putrefaction commences again. Similarly, foods are preserved by chilling or freezing.

The waste products of organisms are often poisonous to themselves, and for this reason fermentations frequently come to an end before the whole of the substance is fermented. Thus neither beer nor vinegar can be obtained of more than a certain strength by direct fermentation, the alcohol or acetic acid checking the growth of their respective ferments. A solution of glucose "set" with the lactic ferment of sour milk will only produce lactic acid to the concentration of about one-half per cent. ; but if chalk be added, the lactic acid will be neutralised as produced, and the fermentation will go on till the whole of the glucose is converted into insoluble calcium lactate.[1] When this is accomplished the lactic ferment dies from want of nutriment, and its place is taken by another organism, of which some germs are sure to be present, which ferments the calcium lactate into calcium butyrate. If the nourishment fails, or the conditions become less favourable for one ferment than for some other which exists even in small quantity in a liquid, the former is quickly overgrown and killed, and the latter takes its place. Thus the ordinary ferment of the bran drench will die out rapidly unless constantly transferred to fresh bran infusions.

Many of the products of bacteria (like those of some of the higher plants) are intensely poisonous both to animals and man. Many of the severe symptoms of disease are caused by these poisons produced in the body. Thus the tetanus-bacteria produce a poison similar in its effects to strychnine,

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[1] For the practical preparation of lactic acid the solution may contain 7½ to 11 per cent. of glucose and some nitrogenous nourishment. The solution should be slightly acid. See *Journ. Soc. Chem. Ind.*, 1897, p. 516.

but even more virulent. Not only are such poisons produced by disease-bacteria in the body, but frequently also in the earlier stages of putrefactive fermentation. The latter are known as *ptomaines*, and when present in cheese and preserved foods are liable to cause poisoning. Such putrefactions are often unaccompanied by any disagreeable odour or flavour.

The fermentations which are most important in the tannery are, firstly, the ordinary putrefaction which attacks hides as well as other animal matter, and which is usually a complicated process carried on by many sorts of bacteria and other micro-organisms. This may be regarded as generally injurious to the tanner ; but it is utilised for depilation in the " sweating " process and in the " staling " of sheep-skins, in both of which advantage is taken of the fact that the soft mucous layer of the epidermis, which contains the hair-roots, putrefies more rapidly than the fibrous structure of the hide itself. In soaking also, use is sometimes made of the power of putrefactive ferments to dissolve the cementing substance of the hide, though in this case with doubtful advantage to the tanner. In the liming process putrefaction makes itself felt when the limes are allowed to become stale and charged with animal matter, softening the hide and finally rendering the leather loose, empty, and inclined to " pipe," but in normal liming bacterial action plays an important part. Here the effect is useful if not carried too far.

In bating and puering the action is almost entirely due to the enzymes and other products of bacterial activity, the original chemical constituents of the dung being apparently of minor importance. Naturally the liquid is adapted to the growth of many other organisms beside those acting most advantageously on the hide, and injury in the bates from wrong forms of putrefaction is very common, if indeed it is not always present in greater or less degree.

In drenching the effect is, at first, entirely due to the weak acids produced by bacterial fermentation of the bran, but becomes complicated in its later stages by putrefactive and other fermentations, which may be desirable or otherwise.

In the tanning liquors fermentation is not so marked, but is of great importance owing to the production of acids by bacterial action from the sugars present in the material. The acids themselves are apt to be fermented and destroyed, principally by the oxidising action of *Saccharomyces mycoderma* and the higher moulds, which also act very destructively on the tannins.

The effect of these acids on the hides is to swell them and to neutralise any lime they may contain. They also give to the liquors a characteristic sour taste, as a consequence of which liquors containing acetic and lactic acids are usually known in the tannery as " sour liquors."

It is doubtful whether the action of fungi is completely stayed even by the drying process. The heating of leather in the sheds is due to bacteria and the higher moulds, and Eitner considers their growth one of the causes of the " spueing " or " gumming " of curried leathers.

From what has been said, it is obvious that, with regard to fermentations, a double problem is presented to the leather manufacturer, since he desires to utilise those which make for his advantage, while controlling or destroying those which are injurious. The first step to a solution of these problems is a more complete knowledge of the organisms which serve or injure us, that we may, as it were, discriminate friends and enemies. We may then approach the question in two ways. Taking the drenching process as an example, we may, on the one hand, introduce a " pure culture " of the right ferment into a sterilised bran infusion, and so induce only the one fermentation which we require ; or, on the other hand, as different ferments are affected in varying degrees by antiseptics, we may perhaps choose such as permit the growth of the organism we want, while killing or discouraging the rest. We may also arrange the nutriment, temperature, degree of acidity, and other conditions so as to favour one organism rather than another. All three methods have been applied in brewing with good results.

Some information on the technique of bacteriology may be found in chaps. xiv. and xv. of *L.C.P.B.*

CHAPTER V

ANTISEPTICS AND DISINFECTANTS

"ANTISEPTICS" are often defined as substances which check putrefaction without necessarily destroying bacteria and their spores, while "disinfectants" are poisonous to ferment-organisms, and actually destroy them; but though great differences exist in the extent of their sterilising power, the whole distinction is one rather of degree than of kind, and has little practical value. Thus common salt is incapable of *killing* most bacteria, even in concentrated solution, though it holds putrefaction in check both by withdrawing water from the hide and by directly preventing the multiplication of bacteria. If the salt be washed out of the hide, putrefaction is at once resumed by the organisms present. Hides, on the other hand, which have once been sterilised by powerful disinfectants, such as phenol ("carbolic acid") or mercuric chloride, do not again putrefy till the organisms which are killed are replaced by fresh ones from outside. The action of sodium sulphate, and many other salts, is similar to common salt in this respect, while a large proportion of the aromatic compounds are permanently disinfectant, though their efficiency varies with the species of bacteria involved.

Biernacki and others have shown that some disinfectants when extremely diluted actually stimulate alcoholic fermentation, *e.g.* mercuric chloride 1 in 300,000, salicylic acid 1 in 6000, and boric acid 1 in 8000, and this is probably true of other ferments, and in many cases organisms become habituated to antiseptics in doses which would at first have proved fatal.

The number of antiseptics available is now so great that it is impossible to give a detailed account of all, but the following are among those which are best known and have been practically employed:—

Lime possesses some antiseptic properties, and is largely used in the preservation of fleshings before they are sent off to the glue factory. They are most conveniently stored in a large vat filled with a strong and fresh milk of lime. Dilute solutions of caustic alkalies have an effect similar to that of lime. One per cent. solution of caustic soda is practically sterile for most bacteria, but when lime liquors have become charged with dissolved organic matter, they support bacterial life ; and this is probably true of other alkaline solutions.

Common salt, sodium chloride, NaCl, acts to a certain extent by its solubility and its dehydrating effect on animal tissues, which removes water from hides and other materials which it is used to preserve. Probably the latter characteristic has a good deal to do with its effect in checking the development of bacteria, since many species thrive quite well in weak salt solutions, and some even in brine, and the dehydrating effect of the salt enables it to harden many animal tissues if used in sufficient quantity, the water they contain running away in the form of brine.

The very considerable antiseptic and dehydrating effect of neutral salts like sodium chloride and sulphate on the hide seems at first sight somewhat inexplicable, and though in the case of the dry sulphate much water is removed as water of crystallisation, this does not apply to common salt, and especially when it is used in the form of brine, since strong solutions have rather a swelling than a dehydrating effect on neutral gelatine, and, presumably, on hide-fibre. The explanation is, probably, that in the early stages after slaughter the skin is always acid from the production of sarcolactic and perhaps other acids, but as putrefaction proceeds it becomes alkaline from the evolution of ammonia. The result is that on the acid skin a slight " pickling " effect is produced (p. 234). No doubt a similar effect, but much less marked, may be produced by the Na′ on the alkaline skin, but this explanation if correct points to the importance of early salting, and it may be suggested that if the skins are already slipping and alkaline, a more preservative effect, and probably an economy of salt, would be obtained by the addition of, say, 2 to 3 per cent. of ground nitre-cake (hydric sodium sulphate) to the salt to restore the acid condition.

Ordinary rock salt frequently contains ferric oxide and sometimes chloride ; and iron, either originally present in the salt, or derived from the action of the latter upon the iron contained in the blood, is one of the causes of what is known as " salt-stains." These are sometimes visible on the flesh of salted hides, but show little during the liming of the hides, unless sulphides are used, when stains appear of a greenish-black, from the formation of sulphide of iron ; and when the hides come into the tanning liquor, black or bluish stains are produced by the action of the tannin, which are partially removed by the acids of the liquors during the tanning process, but generally show to some extent in the finished hide. There are other species of salt-stains, not apparently due to iron, but to the colouring matter produced by fungoid or bacterial growth, which it is practically impossible to remove, and which are stated to be sometimes caused by the use of old salt with which hides have been previously salted.[1] Iron-stains are most readily recognised by the use of a solution of potassium ferrocyanide slightly acidified by hydrochloric acid. If this be applied to the leather, the stains will be changed from a blackish to a blue. A more absolutely conclusive proof is to lay a piece of filter paper soaked in dilute hydrochloric acid upon the stain, and then to test for iron upon the paper with ferrocyanide or thiocyanate. The freedom of the paper itself from iron must be ascertained before use. Iron-stains produced in the salted state are more difficult to discharge than those which are caused later in the tanning process, since iron salts have distinct tanning power, and attach themselves firmly to the untanned fibre. On the Continent, where common salt is heavily taxed, alum, carbolic acid, naphthalene, and other materials are frequently added to it to "denaturise" or render it incapable of being used as food, and these additions are often the cause of trouble to the tanner. Sodium carbonate seems on the whole the best denaturising material.

Sodium sulphate, Na_2SO_4, has little if any disinfectant power in dilute solution, but if used in the calcined form (anhydrous sodium sulphate), as proposed by Eitner[2] as a substitute for common salt in preserving hides, it withdraws water from the hide and crystallises with 10 Aq (about 56 per cent.). This does not run away like brine, but remains in the hide, which retains its weight, and remains plump and swells well in the limes and liquors, as the sulphate is partially converted into caustic soda by the action of the lime; 10 to 15 per cent. on the weight of the hide is sufficient, while salt must be used in nearly double this quantity. Care must be taken that the sulphate used is free from bisulphate, $NaHSO_4$, which has a powerful swelling effect upon the hide-fibre, like sulphuric acid. The neutral sulphate does not redden methyl orange or litmus.

The stronger mineral acids have considerable antiseptic power, even when very dilute, and are of course especially fatal to such ferments as thrive best in alkaline solutions. The use of sulphuric acid in pickling skivers has already been alluded to, and a very dilute solution applied without salt to raw hides prevents putrefaction, though the principal object in using it is to plump the hides and produce a fictitious weight and substance which

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[1] For a further discussion of salt-stains see Chapter VI. p. 36.

[2] Gerber, 1880, p. 185.

disappear on tanning. Such hides of course have a powerful acid reaction to litmus. Sulphuric acid in small quantities has been used with advantage in soaking E.I. kips. A very small excess of hydrochloric acid will sterilise putrid effluents, and no doubt nitric or sulphuric acid would have the same effect. The powerful effect of mineral acids on animal fibre, and their solvent action on cements and iron, preclude, however, their general use as antiseptics.

More important is the use of sulphurous acid and sulphur dioxide, which, from their mild acidity and great antiseptic powers, are capable of a variety of useful applications. Considerable doubt has been raised as to the germicide power of sulphur dioxide, and it is certain that the dry gas is less effective on dry objects than when applied in solution or to moist materials, as is almost invariably the case in the tannery. It may possibly be more efficient in its action on some moulds and putrefaction-ferments than on the pathogenic bacteria which have been most frequently used to test the power of disinfectants ; but in practice it is found extremely useful in the brewery and in gelatine manufacture, and there is no reason that it should be less so in the tannery.

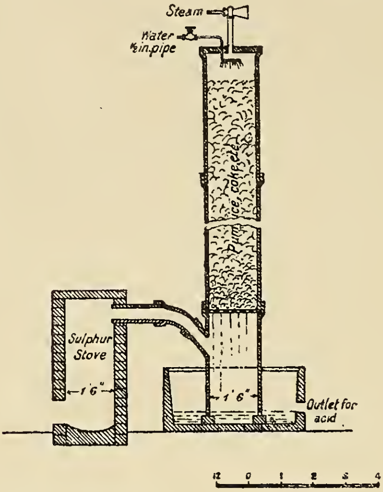

FIG. 5.—Sulphurous acid apparatus.

The gas is most conveniently produced by burning sulphur, which produces double its weight of sulphur dioxide. If used for " stoving " drying rooms and other places infested with moulds, care must be taken to avoid risk of fire. A shallow cast-iron pot set on bricks or sand is generally the most suitable vessel, and the sulphur may be ignited by a piece of red-hot iron or a rag which has been previously dipped in melted sulphur. It is corrosive to metal-work, and bleaches many colours, but does not produce any marked injurious effect on leather, though the sulphuric acid formed by oxidation may, if not removed, ultimately make it tender.

For many purposes a solution of the gas is required, and this is most easily made by burning the sulphur in a small metal or firebrick stove from which the fumes are sucked through a "scrubber," which, on a small scale, is conveniently made of large glazed sanitary pipes, packed with coke [1] or broken earthenware, over which water is allowed to trickle. The lowest pipe has an opening for a branch pipe, which is connected with the stove, and rests on three bricks in a trough or tub, which collects the acid solution and forms a water-seal to prevent the escape of gas. Above the inlet for the gases is fixed a wooden grating, on which the coke rests. The scrubber may be 10 to 15 feet in height, and connected at the top with a chimney or steam ejector [2] to produce the draught. The arrangement is illustrated in fig. 5. Another method is to burn the sulphur in a closed cylinder and to force the products through water with an air-compressor, and this is necessary where the gas is used, as is now commonly done in reducing bichromate solution for chrome tanning (see p. 267).

In place of using a scrubber, the fumes may be blown by a steam injector direct into a tank. This is a very good arrangement for washing and bleaching hair, etc., but where large quantities of solution are required is inferior to the scrubber. Injectors of hard lead or regulus metal should be used, and are less acted on by the dry gases than by the very dilute moist exhaust from the scrubber (see p. 401).

Bisulphites have also strong antiseptic properties. "Bisulphite of soda" (hydric sodic sulphite) solution may be made by supplying the scrubber with solution of soda-ash or washing soda; bisulphite of lime, by using milk of lime or packing the scrubber with chalk or limestone (free from much iron) in place of the coke. In either case a much stronger solution is obtained than with water alone.

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[1] Coke contains a good deal of iron, which will contaminate the acid for some little time. Broken pumice is free from this defect.

[2] The ejector must be of regulus metal to resist corrosion. The air admitted to the stove can be regulated by a brick placed in front of the opening.

Boakes' "metabisulphite of soda"[1] is a very convenient source of sulphurous acid when the latter is wanted in small quantities. It is an anhydrosulphite, $Na_2O.2(SO_2)$, and contains 67·4 per cent. of its weight of SO_2. One molecule of the salt (=190) requires one molecule of H_2SO_4 (=98) to set free the whole of the sulphurous acid. For many purposes the sulphate of soda formed may be neglected and the acidified solution used direct.

For analysis of sulphites and sulphurous acid solution see *L.I.L.B.*, p. 73, and *L.C.P.B.*, p. 13.

If bisulphites are used in tanning liquors, their effect in bleaching and making soluble the "reds" (phlobaphenes) present in many tanning materials must not be overlooked. This action improves the colour of the leather, but at the same time diminishes its solidity and weight, though it probably assists in the more complete utilisation of the tannins. In most "bleaching extracts" bisulphites are present in large excess, and not only keep the "reds" of the extract itself in solution, but dissolve those of other liquors with which they are mixed, and of the leather itself, thus rendering it more porous.

Boric acid, borax, and other *borates* are not very powerful disinfectants. They have no injurious action upon the skin, but to be effective require to be employed in pretty strong solutions, say, 1 per cent., and their comparatively high cost unfits them for general use as antiseptics in the tannery, though boric (boracic) acid is very useful as a drenching and deliming agent (see p. 205, and *L.I.L.B.*, p. 37).

Mercuric chloride, corrosive sublimate, $HgCl_2$, is an extremely powerful antiseptic, preventing the growth of some species of bacteria in solutions so dilute as 1 in 300,000 (Koch). 1 in 14,000 is disinfectant (Miquel), but its power varies very much upon different organisms (Jörgensen states that 1 in 400 is required to kill *Penicillium glaucum*), and it is unsuited for most purposes in leather manufacture, both from its extremely poisonous character, and because it is rendered inactive by various substances present in the materials used. In conjunction with formic acid, however (Seymour-Jones, p. 236), it is extremely effective in the destruction of anthrax spores, and can be employed in solutions so dilute as to be quite harmless to the workmen.

Mercuric iodide dissolved in iodide of potassium solution was patented by Messrs Collin and Benoist as an antiseptic in tanning, but it is expensive, and has the same defects as mercuric chloride; although under favourable circumstances it is even

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[1] Patented by Boakes, Ltd., Stratford, London, E.

more powerful than the latter. Mercuric and copper salts must not be dissolved in zinc or galvanised pails.

Copper sulphate, zinc chloride and *sulphate*, and many other metallic salts are powerful antiseptics, but have only a limited application in leather industries, and do not usually actually sterilise. Copper sulphate is very fatal to *algæ* in water.

Arsenic (arsenious acid), which has been used in curing hides, is an excellent insecticide, but is not effective as an antiseptic ; and sulphide of arsenic (realgar) when used in limes (see p. 189) seems to have little or no antiseptic effect. Arsenious acid is easily soluble in alkaline solutions.

Fluorides have been suggested as antiseptics in the tannery, but have not been much used.

The most important antiseptics at present are those derived from coal tar, and belonging to the aromatic series. Of these, the phenols (carbolic acid, cresol, etc.) are the most used.

Pure phenol, "pure crystallised carbolic acid," is hydroxybenzene, $C_6H_5(OH)$, but the liquid forms which are generally employed contain cresols and higher members of the series, in which one or more of the atoms of hydrogen are substituted by CH_3 groups. These are oily bodies scarcely soluble in water, and even pure phenol is only soluble in cold water to the extent of some 7 per cent. Crude carbolic acid should not be employed in the tannery, since the insoluble oily particles stain the hide, and render it unsusceptible of tanning. Suitable carbolic acid should be of a pale yellow colour when fresh (though it will darken on exposure to air and light), and it should be wholly soluble in a sufficient quantity of water. Its specific gravity should be 1·050 to 1·065. For methods of chemical examination, see *L.I.L.B.*, p. 78. A saturated solution of carbolic acid sterilises hide completely against most putrefactive organisms, but has a sort of tanning effect, adhering obstinately to the fibre so that it cannot be removed by washing ; and hides which have been cured with it cannot be unhaired by sweating, though they may be limed in the usual manner, if somewhat more slowly. Care should be taken in mixing with water or liquor, as undissolved drops will produce the same effects as those of the crude acid. Though heavier than water they frequently float, being sustained by surface-tension. Hides are occasionally stained in this way by salt which has been denaturised with common sorts of carbolic acid. Eitner recommends the use of a solution of carbolic acid in an equal weight of crude glycerine, which readily dissolves in water, and seems to prevent any injurious effect on the hide; but the present price of glycerine is prohibitive.

An aqueous solution containing 1 per cent. of carbolic acid is sufficient for mere sterilising of hides, but if it be desired to preserve them for a long period, stronger solutions (up to 4 per cent.) may be employed.

Quantities so small as 1 part per 1000 control the fermentation of liquors, and prevent the formation of moulds on the surface, economising tannin, and preserving vegetable acids already present, but at the same time lessening their production by fermentation, and therefore sometimes leading to difficulties in the early stages of tanning. Carbolic acid is not, strictly speaking, an acid, but rather of the nature of an alcohol, although it forms weak combinations with bases. It does not swell hides, but is a powerful narcotic poison, and if dropped on the skin in a concentrated form it produces severe burns, which are best treated with oil, while in cases of poisoning oil and chalk must be administered internally, but if the quantity of carbolic acid taken has been large, are not likely to be effective. From its cheapness and efficiency carbolic acid is likely to be increasingly used, although for special uses some of the newer antiseptics have great advantages.

Creasotes and *cresols* can be dissolved in oils and stuffing greases, and act as antiseptics, though less powerfully than in aqueous solution. "Eudermin" is a preparation made for this purpose. Rosin oils and turpentine have also antiseptic properties.

Creasote, "heavy coal oil," or "dead oil," is a complex mixture of hydrocarbons, phenols, and cresols, obtained by distillation of coal tar, heavier than water, and almost insoluble in it. It is largely used as a preservative for timber. "Carbolineum" is an oil of this class, boiling at over 300° C., and intended for application to wood. One or more coats are applied to the dry wood at a temperature of 80° C. The workman's hands must be protected by gloves, as the hot creasote raises painful blisters. Eitner[1] recommends its use for preserving pits, posts, and other woodwork in tanneries. Wood-creasote is a somewhat similar product obtained from wood-tar.

The heavier cresols are so little soluble in water as to be valueless as antiseptics in their ordinary form, but several preparations are made under the names of "Creolin," "Jeyes' fluid," "Lysol," "Izal," "Soluble phenyl," etc., in which they are treated with additions of soap or alkalies, which cause them to emulsify or dissolve in water, generally as milky liquids, which are powerful

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[1] Gerber, 1889, p. 183.

germicides, and have the advantage over phenol of being non-poisonous. 0·1 to 0·5 per cent. solution of creolin will sterilise hides after bating so that no putrefaction takes place in the liquors. Mr J. T. Wood specially recommends creolin for the general purposes of the tannery, disinfecting pits and tubs, and for checking the action of puers and drenches on goods which have gone a little too far, by throwing them into a 0·2 per cent. solution.

Salicylic acid, orthohydroxybenzoic acid, $C_6H_4OH(COOH)$, is now artificially prepared from phenol. It is much less poisonous than the latter and has no smell, which makes it valuable for certain purposes, but is too dear for most technical applications. Many bacteria appear to become gradually habituated to its action, and the same is true of phenol to a less degree.

Salicylic acid is closely related to protocatechuic and gallic acids, and, like these, gives a blackish colour with iron salts. It is freely soluble in hot water, but very sparingly in cold. The addition of 1 to 2½ parts of sodium phosphate, sulphate, or potassium nitrate to each part of salicylic acid greatly increases its solubility. It is more powerful in preventing the development of bacteria than carbolic acid; a solution of 1 part of salicylic acid in 666 of water is said to be equal in this respect to 1 part of carbolic in 200.

Benzoic acid, C_6H_5COOH, though not much employed except in medicine, is a still more powerful disinfectant, and has the advantage of being non-poisonous to human beings.

"*Anticalcium*"[1] is a solution of mixed sulphonic acids derived from cresols, and has considerable disinfectant powers. It also removes lime very effectively, but from its acid character somewhat swells the skin.

"C.T." (coal tar) bate is a grey crystalline pasty mass, with a tarry smell, and is chemically very similar to anticalcium, if not identical with it. Many other coal-tar sulphonic acids have similar properties. These preparations have not much importance for deliming, but may be useful where an antiseptic action is also required.

Naphthols, $C_{10}H_7(OH)$.—These bodies, which have the same relation to naphthalene as the phenols to benzene, are powerful antiseptics; and naphthalene itself appears to have antiseptic power, and is occasionally used for denaturising salt. There are two naphthols, varying in the position of the OH group in the molecule, and denominated α and β, of which α naphthol is the more powerful antiseptic and the less poisonous, though β,

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[1] Gerber, 1895, p. 133.

being cheaper, is the common commercial article. It is said that quantities so small as 0·1 to 0·4 gram of α naphthol per liter are sufficient to prevent the development of microbes, while of β naphthol about ten times that quantity is required.

Naphthols are not very expensive, but their value is diminished by the fact that they are insoluble in water, though soluble in alkaline solutions, but their compounds with bases are of much lower antiseptic value, and the same is true of their alcoholic solutions ; when an alcoholic solution is added to water the naphthol is precipitated, but if an addition of soap or camphor be made to the alcoholic solution, the naphthol remains in a very finely divided condition, if not dissolved.

Adopting a suggestion of Eitner's [1] with regard to oxynaphthoic acid, hides may be sterilised by the naphthols and other difficultly soluble aromatic antiseptics by treatment first with a weak alkaline solution of the antiseptic, and afterwards with a weak acid to remove the alkali. Hides treated in this way are permanently sterilised, and cannot be unhaired by sweating, and would probably lime with some difficulty.

Carbon disulphide.—Moret has suggested an aqueous solution of this compound as an antiseptic, and it seems to have considerable sterilising powers, but from its inflammability, poisonous character, and unpleasant smell, it is not likely to come largely into use. It is sometimes useful for preserving putrescible matter in the laboratory.

Formaldehyde, COH_2, in aqueous solution containing about 40 per cent. of formaldehyde together with a little formic acid, is sold under the names of "formalin," "formol," etc. It has great disinfectant powers, and is valuable in various processes of leather manufacture, but has a hardening and tanning effect on hide-fibre and gelatinous matters, so that in very dilute solution it will produce leather.[2] The vapour of formaldehyde, or of its condensation-product paraform, may be employed to harden microscopic preparations. One part of formaldehyde, and consequently 2½ parts of "formalin" in 12,000 parts of water, is said to sterilise, and forms a good disinfectant solution. Even in considerably larger proportion than the above it is not poisonous, and thus possesses the bactericidal power of sublimate without the latter's poisonous properties. Formaldehyde has another advantage over most, if not all, other antiseptics, in that it may be used as well in the gaseous as in the liquid state, and on that account it is largely employed in the disinfection of rooms

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[1] Gerber, 1888, p. 101 ; 1889, pp. 99 *et seq.* See also p. 206.

[2] Gerber, 1897, p. 67 ; *ibid.*, 1899, pp. 101, 205, 218.

or of articles which would be spoiled if they were to be wetted, as the gaseous formaldehyde, though thoroughly disinfecting them, will not injure the colours of materials of the most delicate fabrics.

On account of its power of rendering gelatinous matters hard and insoluble in water, formaldehyde requires to be employed with great caution in leather manufacture, but 0·2 to 0·3 per cent. may be successfully used in admixture with egg-albumen in the preparation of "seasoning" in the finishing of morocco leather. It is also used commercially to produce different varieties of white leather for soldiers' accoutrements and similar purposes (pp. 459, 576), and for fixing hides in a swollen condition prior to tanning.

Triformol (tri-oxymethylene, "paraform") is a product of the polymerisation of formaldehyde, and is prepared by evaporating a solution of the latter to dryness on the water-bath. It is more powerful than formalin in its antiseptic properties, but has not entered very largely into use as a disinfectant, though considerable use is made of it to "fix" bacteria in gelatine for bacteriological purposes.

Camphor and essential oils, as well as oil of turpentine, are antiseptics, and the cheaper essential oils, such as those of winter-green, black birch, sassafras, and aniseed, are frequently employed, especially in America, in preserving pastes, finishes, and seasonings, and at the same time covering offensive odours. The odour of essential oils becomes much more powerful as they are diluted, and very small quantities suffice for the purposes mentioned. Birch-tar oil, such as is used to give the scent to Russian leather (p. 453), is antiseptic, and prevents the attack of insects. Artificial methyl salicylate is now made, which is chemically identical with oil of winter-green, though from the presence of some impurity it has a different, but not unpleasant, odour. It has considerable antiseptic powers, and is much used as an external rheumatism remedy. The essential oils of cloves and pimento are also good antiseptics.

CHAPTER VI

THE ORIGIN AND CURING OF HIDES AND SKINS

A CONSIDERABLE proportion of the hides and skins used in leather manufacture are those of animals killed by the butcher for food, and these are frequently employed by the tanner without any preliminary curing. Domestic hides and skins are now generally sold by auction in weekly markets in the principal towns, after sorting and classification in weight and quality.[1] This is in many respects an improvement on the old method of purchase direct from the butcher, but it often leads to delay in delivery, and in hot weather hides suffer from putrefaction. In most cases the damage is not sufficient seriously to affect the durability of the leather, but the delicate membrane of the "grain" is injured, and the hide or skin unfitted for coloured leather, or any purpose where small damages to appearance are important. Butchers are averse to the use of salt, because it withdraws water from the hide in the form of brine, and so causes it to lose weight; but much injury would be saved by a light salting, and all hides or skins on which the hair is "slipping" should be regarded as damaged for fine leather manufacture.

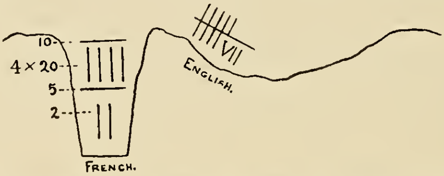

FIG. 6.—Method of marking weight on hides; 97 lb.

Sheep-skins are not usually bought direct by the tanner, but by the fellmonger, who removes the wool; and as this is of much

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[1] The weight of English market-hides as credited to the butcher is usually marked on the edge of the butt near the tail by cuts with a knife, the mode of numeration being sufficiently explained by Fig. 6, in which cuts crossing the horizontal line each represent 20 lb., that above it 10 lb., while less amounts are expressed in Roman figures.

On the Continent weights are usually given in pounds of half a kilogram (50 kilos=110 lb. English). In Paris the marking is on the tail, and is also shown on fig. 6.

greater value than the skin, the latter is frequently handled very carelessly, and its quality sacrificed for the sake of real or fancied improvement to the wool. In very many cases the skin is "sweated" or "staled" by hanging in a warm and moist chamber, heavily charged with ammonia derived from the putrefaction of the skin, until the wool is sufficiently loosened to be "pulled." If this treatment is conducted with extreme care the skin may escape serious injury, but in most cases the grain is weakened, and the foundation is laid of damage, which makes itself felt throughout the tanning process.[1]

The best method is that generally employed by the freezing companies, and to some extent by the more modern fellmongers, in which the skins, after thorough washing, are painted on the flesh side with a thick milk of lime, to which is added 25 to 30 per cent. of sulphide of sodium on the weight of the lime employed, taking care that none of the solution touches the wool. The skins are then piled flesh to flesh for twenty-four hours, when the wool will be found ready to pull. An older method is to use milk of lime only, and in the case of shearlings, where the wool is not of so much value, the skins are laid flesh to flesh in shallow pits and covered with water. For further details see Chapter XIII. on depilation.

One of the great causes of injury to the pelts is their collection by the fellmonger in what are called "gathering limes," where they remain till taken by the pelt sorter. These limes are frequently very old and stale, and swarming with putrefaction bacteria. If kept in limes at all, these should be fresh and frequently renewed, but even fresh sweet limes dissolve the cementing substance of the fibres, and increase the naturally loose texture of the sheep-skin if the treatment is long continued. In the American stockyards the skins are only limed for the time necessary to swell and differentiate the fibre, and are then at once drenched and preserved by pickling (p. 234).

Where hides or skins cannot be used at once in the fresh state, there is probably no better method of preserving them than the use of salt. Although salt is not fatal to bacteria, it so slows bacterial growth, partly by its direct antiseptic effect on many organisms, and partly by withdrawing water from the skin, that well-salted skins can be kept in good condition for an almost unlimited time. Where it is only required to preserve goods for a week or two, a moderate sprinkling on the flesh side is efficient, but if they are to be preserved for a length of time, more thorough

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[1] As to the use of ammonia gas as a substitute for putrefaction see p. 166.

treatment is necessary. It is said that however carefully hides are salted, they deteriorate if kept in this condition above twelve months. It is advantageous to wash and well-drain hides before salting, as by this means most of the blood, lymph, and dung are removed, which are the most putrescible constituents of the hide.

The method of salting employed in the Chicago stockyards for " packer " hides may be taken as a good type of a thorough salting. The hides are first trimmed from useless " switches," and any large portions of adhering fat are removed. The curing takes place in large and cool cellars with concrete floors. The detail is well given in the following extract from the *Shoe and Leather Reporter* :—

" Great care is taken to make the sides of a pack higher than the middle, so that the brine which is made by the juices of the hide coming in contact with the salt will be retained. The brine can only escape by percolation, and hence the fibre of the hides is thoroughly cured. The floor of a hide cellar is usually of concrete, and a pack is from 15 to 20 feet long, and as wide as the space between the posts which support the floor above. The sides of a pack are built first to a height of from 4 to 6 inches ; the cross layers are then put on, generally three on each side, two being inside and one having the butts drawn out to the edge. In a pack 20 feet long the side layers will contain about 25 medium-sized hides each, and a cross-layer 12 or 14. To begin a pack a truck-load of hides is run along to the front of the place selected, one spreader grasps the butt and his partner the head of a hide, and together they carry it to what is to be the rear of the bed. The hide is then dropped, so that the folded back is parallel to and from 15 to 20 inches from the inside line of the posts, the head a trifle closer than the butt. The front man takes the dewlap and front shank in his left hand, and extends his right along the belly of the hide as far as is necessary to raise the edge, the rear man holding the flank with one hand and the hind-shank with the other. They keep their legs well out of the way of the salt thrower, who with a single throw covers the whole hide, being particular that enough salt strikes against the edges held by the men to make a pronounced ridge when they are lapped down. A little salt is thrown on the hair surface and the butt folded over about a foot. The folded edge is then drawn out even with the outer line of the pack. More hides are placed the same way until the corner is high enough. After this, each hide is put further forward to make a level surface from rear to front, the heads at the front corner being folded back as the butts were at the starting place. The other side is built the same way, and then the cross layers are put on alternately until the pack is level, when sides are again built as before. In putting on the first hides of the cross layers they are thrown over the edge, to lap back again when the salt is thrown on ; the layer is then continued on to the front. The spreader who holds the butt does the guiding in every case. He drops the butt down at exactly the proper place, takes the upper flank and shank in each hand, sets one foot on the lower shank to keep it firm, and throws the one in his hands from him with considerable force. The man at the head watches his partner, keeps the folded hide taut, and drops it at the same time as the latter. He takes the fore-shank at the knee in the one hand and the upper headpiece in the other, and setting his foot on the lower side, throws the upper side forward simultaneously with the rear man. Two expert spreaders, accustomed to working together, spread a hide at a single throw, but some little straightening has to be done by hand before the hide is ready for the salt. A gang composed of two spreaders, one salt thrower, and a salt trucker put down forty hides an hour. When gangs are doubled, two men do all the spreading ; the other two place the hides where they can be got at conveniently. A double gang put down eighty hides an hour. The salt trucker brings the salt to the pack in box-trucks, open at one end to permit the entrance of a shovel. The salt thrower keeps the edges and corners of the pack full of salt. He must see that every part of the flesh side is well covered. Each hide takes two scoop shovelfuls of ground rock or coarse white salt, mixed with an equal quantity of old or second salt. The salt thrower throws the shovel forward and to one side and back again with a peculiar swinging jerk, causing the salt to fall regularly over the entire surface of the hide. The ease and rapidity with which a gang operates depends greatly upon the efficiency of the salt thrower. When the pack gets too high to be comfortable for the men, it is brought to a dead level and covered over with clean salt. It then presents a very neat and workmanlike appearance. When the temperature is kept at an even average, two weeks is ample time to cure the hides.

" In ' taking up,' two men strip the hides from the pack. As they were put down from the rear to the front, they are taken up in the reverse direction. No matter how much loose salt is lying on the top, the man knows exactly where to place his hand on a shank ; as the hides are moved forward, the loose salt is thrown off toward the front. One man takes away the salt as it accumulates and trucks it to the salt bins, where it is mixed with new, to be used again. A 'horse,' made of a network of scantling about 3½ feet wide by 6 feet long, and standing 2½ feet from the floor, is placed in front of the pack; on this the hides, flesh side down, are shaken to remove the salt that is clinging to them. This process requires four men, one at each corner. The hide is brought down heavily on the horse twice, and then spread on the floor flesh side up for examination by the inspectors, of which there are two, one representing the house and the other the buyer of the hides. They sweep off any salt that may be left, and examine for cuts, sores, brands, manure, and grubs. They also see that the hide is properly weighed and classified. If the contract calls for a special trim it is now done. Two men then roll the hide, beginning by lapping over the shanks, head, and neck. Then the sides are folded over and lapped again, leaving the roll 15 to 18 inches wide. The ends are thrown inward, slightly overlapping each other; a final fold is then given, and the hide is ready to be tied. Rope the size of clothes-line is used for tying, and is cut into lengths of about seven feet. It takes three men to tie for a gang such as we have described. After tying, the neat bundles are weighed and loaded on the cars for shipment. A small tare is allowed the buyer."

About 25 per cent. of salt on the green weight of the hide is required for thorough curing. Rock salt, merely crushed, is frequently used, but this is very liable to contain iron in the form of ferric oxide, which is said to be the cause of the peculiar marbled or map-like markings known as salt-stains. These certainly contain iron, as is shown by their brownish-yellow colour when the hides are unhaired from a white lime, their dull green from sulphide limes, and the fact that they turn black or purplish in tan liquors, and give the ordinary blue with ferro- and ferricyanides, and it is certainly better to use crystallised salt, but its use does not always prevent them, and their cause is probably more complex, and not unconnected with bacterial action. In 1912 it was the subject of considerable investigation by Dr Abt, Professor Becker, and others, the results of which will be found in the volume of *Collegium* for that year, but unfortunately these authorities do not altogether agree in their conclusions, and it is possible that they were not dealing with the same defect, as probably various stains of different origin are confused under the general name. Abt found that the stains which he examined appeared to originate on the flesh side and spread through to the grain. He attributed them to the small spherocrystals of double sulphate of calcium and sodium (Schlott's grains) which occasionally occur in salt, and which he sometimes found adhering to the spot where the stains originated. The stained parts did not usually contain more iron than the rest of the unstained skin, but, singularly, had a large excess of phosphoric acid, which is not contained in the salt. He produced similar stains artificially by placing on the flesh side grains of calcium sulphate with crystals of ammonium phosphate, and their appearance was favoured by the addition of traces of iron salts. He attributes the phosphoric acid (probably in the form of ammonium phosphate) to bacterial action on the nuclei of the epidermis and hair-sheaths, and the iron may be derived in sufficient quantity from the hæmoglobin of the blood left in the skin. He admits that the colour-reactions with sulphides, tannin, etc., are due to iron, but cannot explain why the unstained parts, which contain sensibly as much iron, do not stain. He found no microscopic evidence of bacteria in the stains, and attempts at culture gave negative results.

Becker, on the other hand, found in the ochre-yellow stains *cocci* of about 1·5 μ diameter, which he cultivated easily on meat-broth peptone gelatine, and which were aerobic (required oxygen), and liquefied the gelatine, and gradually liquefy hide. He also detected *coccus* bacteria in the red and orange stains, but these did not liquefy gelatine or attack hide, and may be considered harmless to the tanner. They were also cultivated on bouillon-peptone gelatine, but with considerable difficulty, requiring a somewhat high temperature and a long time (about six weeks) for their development. With all three bacteria Becker found a *torula* or yeast, with which they appear to be symbiotic. The red and orange bacteria could be cultivated alone on raw hide containing blood and lymph, but not on pelt, from which these liquid nourishments had been removed by the wet-work, but developed on the latter when associated with the *torula*, of which the dead cells furnished them with nourishment. Becker considered that salt alone is not sufficiently antiseptic to prevent the growth of bacteria, but found that an addition of not less than 4 per cent. on the weight of the salt of calcined sodium carbonate rendered it practically sterile. He also found that soaking the hides in a 0·25 per cent. solution of zinc chloride for two hours, or in a 0·5 per cent. solution for half an hour, previous to salting had a similar effect. He stated that 1·5 per cent. addition of sodium perborate to the salt would sterilise but swelled the hides, and recommends soaking for an hour previous to salting in a 0·25 per cent. solution of artificial mustard-oil, but points out that the hands of the workmen must be protected by india-rubber gloves.

The writer has from time to time examined many salt-stains of the map-like kind which appear on the grain, but has never paid much attention to the flesh, nor seen signs of serious injury there. These marbled or map-like stains, whatever their original cause, always owed their colour to iron, and gave the usual iron-reactions. In this connection attention may be drawn to the case of plaster-kips mentioned on a later page. Although much iron was contained in the salt-earth which constituted the cure, serious staining only took place after the kips had been kept through a winter in a damp London warehouse, and the iron-tannage of the grain was then so bad as to render the unhairing very difficult and imperfect. In this case there was little doubt that the iron was derived from the cure; but the writer has also observed marked iron-stains following the course of a vein containing blood, which is quite common in kips which have died from natural causes, and which are known as " dead " in distinction from " slaughtered."

It is impossible to anyone who has known them to doubt the care, accuracy, and competence of both Abt and Becker as chemists and bacteriologists, and it is much to be desired that some explanation should be found of their differences, though it may be feared that the effects of the war have rendered co-operative work for the present impossible. It may be that they were working on distinct kinds of stain, but it is not impossible that iron may have accumulated in the spots in consequence of the presence of phosphoric acid, with which iron forms a very insoluble compound, or, on the other hand, that Becker's bacteria owed their colour to iron. Bacteria are well known which absorb iron. The writer has a well on his premises which contains a trace of iron bicarbonate together with calcium and a little sodium bicarbonate, and its walls are always covered with a red-brown deposit of a special iron-bacterium. Though Abt does not specifically say so, he apparently made his analyses of the stained and unstained portions from the flesh side of the hide, and it is not improbable that the iron was simply attached to the unstained portions in an insoluble form (oxide or carbonate), while in the spots it had become soluble and diffused into the hide. These, however, are speculations, and must wait further investigation.

A reddening of the flesh side is often noticed in hides which have been kept in salt long or under unsatisfactory conditions, and is very frequent in wet-salted South American hides. Such hides are said never to produce so firm a leather as those which are sound. This may be due to one of Becker's pigment bacteria. It is also conceivable that it may be caused by *B. prodigiosus*, the bacterium which causes red bread, etc., and which is known to attack pickled skins.

Hides are frequently cured by steeping in salt brine instead of strewing with dry salt. This method is principally resorted to in order to give fictitious weight. Brined hides do not plump well in tanning, the leather is not so good in quality as from those salted with dry salt, and the cure is much less efficient.

Many hides are not only salted but also dried in order to preserve them. Not much detail has been published with regard to the methods used, which no doubt vary much in different places, but probably in some cases the hides are salted in pile and in others by brining, and then hung up to dry. The principal object of drying is to economise weight and cost of transport, but it makes the hides much more difficult to wash and soften for tanning (though easier than hides dried without salting), and probably the crystallisation of the salt has a weakening effect on the fibre. Hides cured in this way are styled "dry-salted."

A large number of the hides of the small native cattle of India are imported into this country in a dry-salted condition. The following particulars of their cure are taken from a paper by the Author and Mr W. Towse.[1]

Dry-salted, or, as they are commonly called, "plaster cures," such as those of Dacca and Mehapore, are thickly coated with a white material, which in the first instance is merely the insoluble portion of a saline earth used in the cure; though in many cases it is applied in larger quantities than necessary, with the simple object of giving weight. The salting is thus described by Mr W. G. Evans, who some years ago had considerable experience as a tanner at Cawnpore:—

"The salt used by the natives is a salt-earth, and is so called by them. It is found extensively in the districts of Cawnpore, Agra, Delhi, Lucknow, Patna, etc., and has no doubt something to do with the localisation of the hide-curing and kindred industries in these places. The mode of procedure used is pretty much as follows: the salt-earth is mixed into a very thin paste, and this is lightly brushed on to the flesh side one day, and the hide allowed to remain over night under cover. Next day, for best hides, the same solution is again spread on the flesh side of the outstretched hide and rubbed into it with a porous brick, and then, for legitimate salting, the hide is allowed to dry under

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[1] *Journ. Soc. Chem. Ind.*, 1895, p. 1025.

cover. If for export, the saltings may be three or four, and the hides are treated out in the open, subject to the intense heat of the sun ; which accounts for the number of hides which go back in the soaks in England and elsewhere. We had a clause in our agreement with hide-factors, that any hides which did not come down to natural suppleness in two days in clean water were to be returned. Of arsenic curing I know nothing, and it is not so much in vogue as formerly. There is quite a trade in Cawnpore, Lucknow, Allahabad, etc., in treating old and inferior hides with new for export, and great efforts are made by native holders to get their stocks down before the rains commence, as they say, and rightly I think, that hides are not worth so much after the rains by 30 per cent. The peculiar latent moisture of the rains affects them very detrimentally."

Under certain circumstances this mode of cure gives rise to extensive iron-staining of the skins, and analyses of the material scraped off Dacca and Mehapore kips were undertaken with a view to elucidating the causes of this injury. The following are the results of the analyses referred to, which were made upon the residue after the rather considerable quantity of fibrous organic matter, which had been scraped off with the cure, had been destroyed by ignition, together no doubt with traces of ammoniacal salts :—

	Dacca. Entire Cure.	Mehapore. Entire Cure.
Sand and silica	20·55	27·38
Fe_2O_3	2·77	1·86
Al_2O_3	2·48	2·74
Mn_3O_4	0·60	0·40
CaO	2·60	3·70
MgO	3·38	3·69
Na_2O	28·97	26·80
SO_3	38·90	33·75
Cl	0·22	0·18
H_3PO_4 and CO_2	Traces	Traces
	100·47	100·50

The soluble salts of the Dacca cure were also analysed separately with the following result :—

CaO	0·70
MgO	0·60
Na_2O	29·00
SO_3	37·90
Cl	0·22
Moisture	32·12
	100·54

It thus consisted exclusively of sulphates, with a mere trace of chloride. The cures, after ignition, were both neutral to phenolphthalein, but before ignition the Dacca was distinctly alkaline, in consequence probably of the presence of ammonium salts, and both showed considerably larger traces of carbonates before than after.

The most striking feature of these analyses is the absence of chlorides. The cures are thus practically free from common salt, and owe their antiseptic power to the sodium sulphate which they contain, and which indeed forms their principal constituent. Nitrates appear to be entirely absent. Sodium sulphate sometimes forms large crystals in pits used for soaking these kips.

The iron-staining of hides which has been mentioned appears to result only when the hides after cure are exposed for a lengthened period to a moist atmosphere, in which the carbonic acid present probably also plays its part, the iron passing into solution as hydric carbonate.

The analyses show a striking resemblance to those of the soda deposits of Wyoming, given by Dr Attfield,[1] except that their percentage of sodium carbonate is smaller, which is quite intelligible in the light of Mr Brunner's abstract on the "Probable Origin of Natural Deposits of Sodium Carbonate,"[2] which supports the view that the sodium carbonate is derived from sodium sulphate by the reducing and carbonating action of low organisms.

It may be noted here that the preservative properties of sodium sulphate are well known, and the anhydrous sulphate has been recommended as a substitute for common salt (see p. 23).

Drying is a very common method of preserving hides as well as other putrescible matters. It has no effect in killing bacteria, but putrefaction can only go on in presence of a considerable amount of moisture. As applied to hides, it is, to the tanner, one of the least satisfactory modes of cure, involving very considerable difficulties in bringing hides back to the moist and swollen condition which is necessary at the outset of his operations, but it is the only practical method in districts far from the coast and with primitive modes of transit, both on account of the cost of salt and the lessened weight of the dried hide. Great differences are found in the ease with which dried hides soften, according to the way in which the drying has been accomplished, the difficulty being greater the higher the temperature which has been used (see p. 159). The best mode of drying is to hang in the shade in a good draught of cool air, with the flesh side out.

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[1] *Journ. Soc. Chem. Ind.*, 1895, p. 4.

[2] *Ibid.*, 1893, p. 116.

Hides or skins dried in a tropical sun are not only difficult to soften, but are liable to damaged portions, which either refuse to soften or blister and go to pieces in liming, owing to the structure of the hide being destroyed by heat, the outer surface drying first and forming an impervious layer which hinders evaporation from the inside, so that the moist interior becomes melted, while the outside appears quite sound. Such injuries are often only to be discovered by soaking and liming. Very similar damage may occur from putrefaction of the interior after the outside has become dry, and to get good results the drying must be gradual, but rapid, especially in hot climates. South American hides are mostly dried in the sun, suspended by head and tail from stakes, with the hair side out.

The risk of injury by putrefaction during drying is diminished by the use of antiseptics. Solutions of arsenic have been frequently used for this purpose, and many of the dried Indian kips are of what are known as "arsenic cures," although the writer has never been able to detect arsenic in any which he has examined, and its use seems by no means general. The arsenious acid is usually dissolved in soda solutions. Such solutions have little antiseptic power even if strong, and are mainly useful in preventing the attacks of insects, which are often very destructive. The larva of a small beetle, *Dermestes vulpinus*, frequently devours the whole fibrous tissue of patches of the hide, leaving only the epidermis.

It may be well here to say a few words about the injuries and defects to which hides and skins are liable, although some of them are not strictly due to the cure. The most serious, and yet preventable, injury is that due to butchers' cuts. As the value of the hide bears only a small proportion to that of the meat, many butchers do their work extremely carelessly, and this is encouraged by the loose classification of "damaged hides" in some markets. There is also an idea that the appearance of the meat is improved by a thin layer of the white skin-tissue being left on it, and, for this reason as well as mere carelessness, butchers frequently score the flanks of the hide with shallow cuts, which greatly diminish its value. The "packer hides" of the United States, and the products of the large saladeros or slaughtering ("salting") establishments of South America, such as Liebig's, show what can be done by skilled work in this respect. In the United States, much of the flaying is done by means of a wooden cleaver instead of a sharp knife. Another method to some extent in use, and which may be recommended for calf- and sheepskins, is to inflate the carcase before skinning with air from a compressing syringe, which tears the connecting tissue between the skin and the body, and renders flaying much easier.

Brands are a great source of damage to hides, but where cattle roam at large on unfenced plains, as on the prairies of Texas and the Pampas of South America, it seems indispensable for the recognition of ownership, no other mode of marking being sufficiently permanent and conspicuous. It is unfortunate that, as the animals crowd together, and cannot be closely approached, it is necessary that the brands should not only be large, but placed on the most valuable part of the hide. Generally on the Pampas an effort is made to keep them on one side only, so that in South American hides it is possible to select clear and branded sides. In the United States much land is now fenced with barbed wire, which, while it obviates the necessity of branding, introduces another evil in the form of "barbed wire scratches," which are frequently troublesome in "packer hides."

Tar-brands may also cause considerable injury to the grain, especially if applied with a very hot iron, though it is much more superficial than that of those actually burnt into the skin.

In countries where cattle are used for draught purposes goad-marks are a frequent source of injury, and some of the large cattle-ticks do considerable damage to the hides of Spain and South America. From the tanners' point of view, however, the most injurious insects are the "bot-flies" or "warble-flies" (*Hypoderma bovis* and allied species, fig. 8). There has been much controversy as to how the eggs of these insects are deposited. In the horse bot-fly it is known that the eggs, first deposited on the skin, are licked off and swallowed by the animal, and develop in the stomach, where they pass their larval and pupal life hanging on to its interior coats, and only drop off and are passed out with the dung before their final change to the complete fly. Fortified by this, and by some direct observation, some American naturalists have been for some years of opinion that the American species at least hatches in the stomach, and as a minute larva wanders through all the intervening tissues till it reaches the skin, where it undergoes its further development. The late Miss Ormerod, who made a careful study of *Hypoderma bovis*,[1] believed

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[1] E. A. Ormerod, *Some Observations on the Œstridæ*, Simpkin & Marshall, London, 1884.

Prof. Clement Vaney, Reports of the Association Française pour la Destruction du Varron, Paris, 1910–1911 : *Le Développement de l'Hypoderme du Bœuf*, and *Les Varrons d'hiver*, Goury, Paris, 1911.

Dr Hans Gläser, *Mittheilungen des Ausschusses zur Bekämpfung der Dasselplage*, Nr. 3–6, Berlin, 1912–14.

Department of Agriculture and Technical Instruction for Ireland :

that the egg was laid on the hair of the back, where it hatched, and the minute larva simply ate its way below the skin. In 1914 the true life-history is believed to have been discovered simultaneously by Carpenter in Ireland, Seymour-Hadwen in Canada, and Gläser in Berlin, and is even more extraordinary. The flies never strike on the back, where the maggots are found, but on the fetlock or joint below the knee, anatomically the heel of the animal. The *H. bovis*, the more common English species, lays single eggs, while the *H. lineata*, more frequent in America, lays them in single rows, but otherwise almost like the grains in an ear of corn. The minute maggot, at first only about $\frac{1}{30}$ inch long, bores its way through the skin, and wanders through the tissues till it reaches the skin of the back, where it passes its final larval stage, often pausing on the way for a time in the wall of the gullet, where it is frequently found from September to January.[1] It then bores a hole through the skin, enlarged to obtain air for its spiracles or breathing holes, which are in the tail. As it grows it continues to irritate the lower part of the cavity with hooked mandibles, and lives on the pus and matter so produced. It grows to a length of fully $\frac{3}{4}$ inch, and the cavity (fig. 7), situated between the skin and the subcutaneous tissue, is often as large as half a walnut. It remains in the sac only during its larval stage, and falls out on the ground before completing the change to the pupal state, and seeks shelter in the soil or under grass, emerging in about six weeks as a fly. Gläser, with characteristic German thoroughness, allowed one to bore through his trousers into his leg, and finally recovered it from his mouth! The *H. bovis* is shown in fig. 8, and the *H. lineata*, which is somewhat smaller, and the eggs, in fig. 8A. The tail-

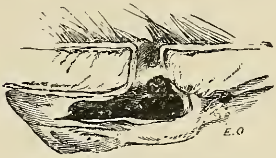

FIG. 7.—Sac of warble, showing growth of epidermis round aperture.

Prof. G. H. Carpenter and others, Reports on "Warble Flies," No. 4, July 1910; *Journal*, No. 2, Jan. 1908; No. 4, 1910; No. 1, 1915. Dublin.

Carpenter and Hewitt, *Some New Observations on the Life-history of Warble Flies*, Thom & Co., Ltd., Dublin, 1914.

Department of Agriculture, Canada, Health of Animals Branch: Dr Seymour-Hadwen and others, Bulletin No. 16, 1912, and No. 22, 1916. Government Printing Office, Ottawa.

Canadian Entomological Society, Report No. 36, 1916.

See also an excellent and well-illustrated article by A. Seymour-Jones, *Leather Trades Year-Book*, 1921, p. 169.

[1] This is less difficult than might be imagined, as the path is mostly through the loose areolar tissues which surround most of the internal organs.

end of the former is covered with orange-yellow hairs, while in the latter they are lemon-yellow.

As regards preventive measures, the most certain is to destroy the grub before it emerges, either by squeezing it out, or extracting it with forceps, and this should be done at intervals from May to August. The method is not very rapid, and it took about six years to completely exterminate the fly on a small island taken for experiment on the Irish coast. No dip or application yet found seems to prevent the fly from striking, and though some of the washes which have been tried do kill the grub, they mostly injure the skin and destroy the hair. The most effective and least injurious seems to be a solution of nicotine, with which the Board of Agriculture and Fisheries are making further experiments.

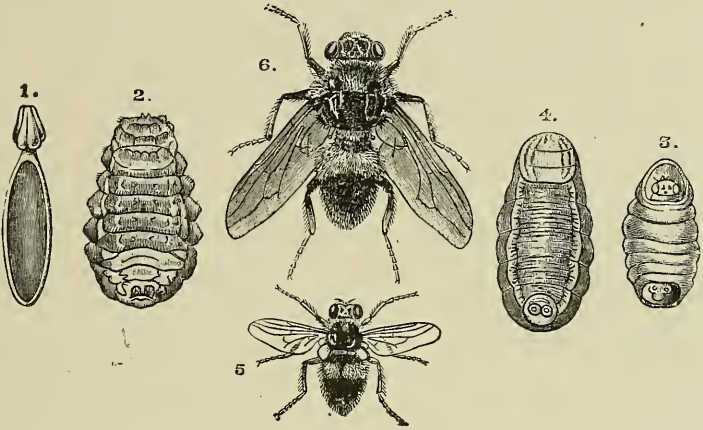

FIG. 8.—*Hypoderma bovis.* 1, egg, magnified about 12 diameters; 2, maggot; 4, chrysalis case; 6, fly, magnified (Brauer); 3, 5, chrysalis and fly, natural size (B. Clark).

In small numbers the warble seems to do little injury to the health of the animal, though it must damage its condition to some extent, and cases have been known where animals have actually died of the inflammation produced. Some idea of the extent of the plague may be realised from the statement that an Indian kip in the museum of the Leeds University Leather Department has not less than 680 warble-holes, and that almost equal numbers have been counted on English hides. Warbled hides are useless for many of the purposes to which leather is applied, and the aggregate annual loss on the hides alone is estimated at not less than £500,000. Another way in which damage is done is by the state of terror which the attack of the fly causes in herds of cattle, causing them to "gad" or gallop aimlessly about. This is the more singular, as the laying of the egg produces no pain, and cattle can hardly be supposed to foresee its result, but the attack of the fly is very persistent, and cattle are sensitive to touches on the leg. Some protection is afforded if the cattle can get in the shade, as the fly seems only to strike in sunshine, and cattle also take refuge in water, where the fly does not pursue them, and where the lower part of the leg is protected.

Deer and goats, and occasionally horses, are attacked by the warble fly, but sheep seem to be exempt, though they are subject to other ills too numerous to mention; but reference must be made to two which affect the skin—cockle and colt. These can hardly be said to be diseases, except from the tanners' point of view, as they neither cause pain nor affect the health of the sheep, though they deteriorate the value of its skin.

Cockle is described by Seymour-Jones [1] as "a disturbance of the pelt structure, resembling a hard pimple or boil of a marked and well-defined appearance, dark in colour, especially after liming, and turning to a deep brownish-black in the tan liquors. The area covered varies in different skins according to given conditions. The markings range in regular waves or ridges from the spine outwards, commencing in the region of the neck and shoulder (*i.e.* the heart), and sometimes covering the whole skin, but frequently ceasing with the ribs." (The name is derived from the shell-like form of the markings.)

"After depilation the cockle assumes a yellow colour, which deepens in tint as the operations succeed each other, and may easily be taken for a species of gristle."

"In mild cases the wet-work treatment will remove the earlier forms, but when the cockle is of long standing, no treatment at present applied will remove them."

Cockle begins to appear about December, and increases until the sheep is shorn, when it entirely disappears. Seymour-Jones had the right-hand side of fifteen sheep shorn, and when slaughtered three days later, the cockle had almost disappeared on the shorn side, though it was marked on the other. These sheep were also subjected to different feeding: five fed with extra oilcake and dry foods displayed cockle in its worst form, five with oilcake alternated with mangolds showed it in medium

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[1] Seymour-Jones, *The Sheep and its Skin*, Leather Trades Publishing Co., 1913.

degree, while five fed with roots and moist food showed it only mildly. It is evident, therefore, that cockle is much influenced by the feeding, and is much increased by the intensive feeding now generally adopted to prepare sheep earlier for the market.

A fatty scurfy deposit appears on the cockly skin under the wool. At Seymour-Jones' request the writer made what chemical examination he could of a very small sample, unfortunately insufficient for any complete analysis. The fatty portion appears to consist of a mixture of glyceride fats partially oxidised, with some cholesterol fat possibly arising from the sebaceous glands and unsaponifiable by caustic potash, though it is saponified, or at least emulsified, by steapsin, one of the pancreatic ferments. Seymour-Jones believes the disease to be connected with the extra demand for fat made by the rapid growth of the wool during the winter season, though the exact mechanism of the process is not very clear.

"Colt" or "dead-fat" in sheep-skins is another trouble very possibly increased by the present intensive feeding, and is an accumulation of fat in the skins, which Seymour-Jones attributes to an adipose degeneration of the fat-cells, probably leading to hydrolysis of the fat and crystallisation of the fatty acids set free.

FIG. 8A.—*Hypoderma lineata.*

CHAPTER VII

STRUCTURE AND GROWTH OF SKIN

ALTHOUGH, at first sight, the skins of different animals appear to have little in common, a closer examination shows that all the Mammalia possess skins which have the same general structure, and thus a general anatomical description of the skin of an ox applies almost equally to that of a sheep, goat, or calf, though on account of the difference in texture and thickness the practical uses of these various materials may differ widely. The skins of lizards, alligators, fishes, and serpents differ from those of the higher animals, chiefly in having considerable modifications in the epidermis, so that it becomes harder and forms "scales," and the arrangement of the fibres presents considerable difference. In many fish-skins, for instance, the fibres are in successive layers, at right angles to each other and diagonal to the skin, like the threads in a "Palmer" tyre, but not interlaced.

In its natural condition the skin is not merely a covering for the animal, but at the same time an organ of sense, secretion and excretion, and hence its structure is somewhat complicated. It consists of two principal layers, the *epidermis* (*epithelium*, cuticle) and the *corium* (*derma*, *cutis*). These are totally distinct, not only in structure and functions, but in their origin. In the egg of a bird and the *ovum* of a higher animal the living germ consists of a single cell, which, as soon as fertilised, begins to multiply by repeated division (*cp*. Chapter III.). The mass of cells thus formed early differentiates into three distinct layers, from the upper of which the *epidermis* arises, the *corium*, together with the bones, muscles, and cartilages, is derived from the middle one, and the lower furnishes the epithelial lining of the internal organs. This distinction of origin corresponds to a wide difference of both anatomical and chemical characteristics. The upper and lower layers are formed of cells, of which the walls mostly consist of keratins, and which multiply by division, while the structures derived from the middle layer consist largely of connective tissue, and yield gelatine and allied substances by boiling, and though produced by cells, are not themselves cellular.

A diagrammatic section of skin is shown in fig. 9, but for the actual microscopic appearance of its various parts the reader is referred to the very beautiful photomicrographs given by Mr A. Seymour-Jones in his series of articles on the "Physiology of Skin" in the *Journ. of the Society of Leather Trades Chemists* (beginning in September 1917, and continued at intervals to the present time), and one of which is by his permission used in illustrating the present chapter.

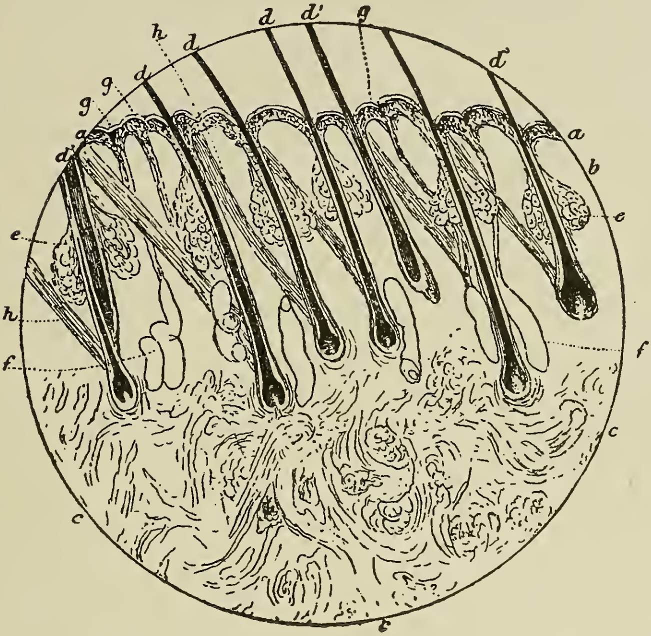

FIG. 9.—Vertical section of calf-skin, magnified about 50 diameters. *a*, epidermis; *b*, grain or papillary layer; *c*, fibrous layer of skin; *d*, hairs; *e*, fat-glands; *f*, sweat-glands; *g*, opening of ducts of sweat-glands; *h*, hair-muscles. Only a small part of the coarsely fibrous part of the *corium* is shown, and it extends somewhat farther upwards than is shown in the drawing.

As will be seen from fig. 9, the upper, or *epidermis* layer is very thin as compared with the *corium* beneath it (the whole of which is not included), and it is entirely removed in the process of depilation, but it is yet of importance to the tanner, since the hair and fat- and sweat-glands, although rooted in the *corium*, are all products of the *epidermis*, and their complete removal depends on its chemical and anatomical character, and its difference from that of the *corium*.

The *corium* [1] consists mainly of a mass of felted fibres of white "connective tissue," consisting of collagen, which on boiling takes up water, and is converted into gelatine. In its lower part, constituting the bulk of the hide or skin, these fibres are comparatively coarse, and are made up of bundles of much finer fibrils bound together in some way, but in the thin upper layer, which the tanner distinguishes as the "grain," the texture is much finer, the bundles appear to be split up into their individual fibrils, and are to a considerable extent mixed with a network of the so-called "elastic" or "yellow" fibres, which are insoluble in hot water, and quite different chemically from the "white" collagen fibres. The hair-bulbs, with their sebaceous glands and sheaths of *epidermis* cells, mostly pass completely through this grain-layer into the coarser tissue beneath, which may be well distinguished as the *pars fasciculi* or "bundle layer."

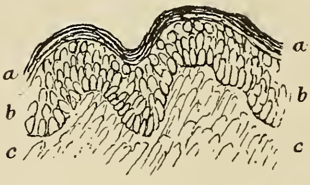

Fig. 10.—Epidermis layer.

The *epidermis* is shown in fig. 9 at *a* and in fig. 10, at *a* and *b*, more highly magnified. Its inner mucous layer *b*, the *rete malpighi*, which rests upon the *corium c*, is soft, and composed of living nucleated cells, which multiply by division, and form cell-walls of keratin. These are elongated in the deeper layers, and gradually become flattened as they approach the surface, where they dry up and form the horny layer *a*. This last is being constantly worn away, thrown off as dead scales of skin ("scurf"), and as constantly renewed from below by the multiplication of the cells. It is from this epithelial layer that the hair, as well as the sweat- and fat-glands, are developed. The *epidermis* is not supplied with blood- or lymph-vessels, so that its cells are nourished entirely from the juices of the *corium* on which it rests, and hence die as they are pushed away from it by the younger cells. The human *epidermis*, especially on the soles of the feet and the palmar surface of the hand, is much thicker than that of most domestic animals, and much misapprehension has been created by the supposition that drawings of these thicker parts represented the usual proportions of animal skin. Indeed in one of the older tanning manuals

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[1] *Corium* (Lat.) or *Derma* (Gr.) each signify both hide and leather, and presumably, when used for hide, include the whole hide which is made into leather, and are synonymous with pelt (Fr. *Cuir en tripe*, Ger. *Blösse*). *Epidermis* is the layer which lies *upon* the *derma*, and therefore *above* the grain.

such a representation of human skin, originally taken from a drawing of the German histologist Kölliker, was boldly labelled "section of calfskin"! In these thick parts of the human *epidermis* the ducts of the sweat-glands take a spiral course which cannot usually be noticed in the sections of animal skin, and many histologists have divided it into several layers, *strata mucosum*, *lucidum*, and *corneum*, which are really only successive stages of development and decay. The *stratum lucidum*, a translucent layer between the mucous and the horny layers, deserves a passing mention from its analogy with the action of the sebaceous glands. As the cells degenerate and dry up they become saturated with an oily matter, eleidin, which they secrete, and so are rendered more transparent. Similarly, the cells of the sebaceous glands, as they are pushed inwards and away from the *corium* tissue with which they are surrounded, and from which they derive their nourishment, become degenerated and break down, and discharge their fatty contents into the cell,

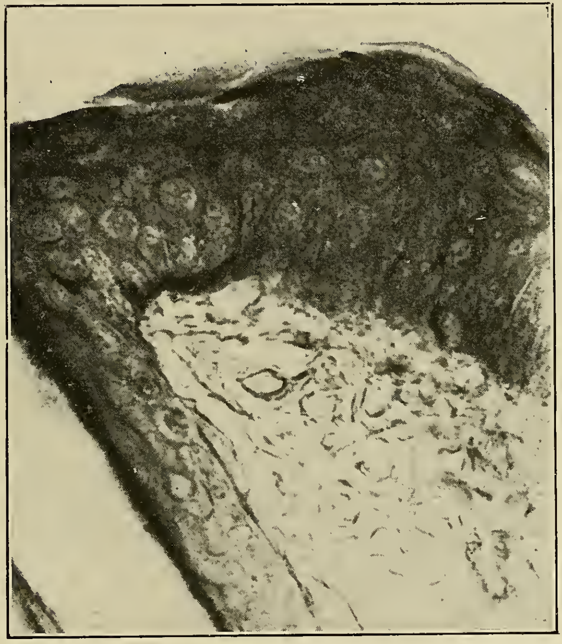

FIG. 11.—Section of calf-skin, showing flattening of epidermal cells. (×720.) Photograph by R. H. Marriott.

and ultimately into the hair-sheath, where it lubricates the hair.

The hair is derived from the *epidermis*, and is contained in a sheath of nucleated cells, which is continuous with the *epidermis* and completely surrounds its bulb, so that it is altogether an *epidermis* product, though rooted deeply in the *corium*. The hair itself is covered with a layer of overlapping scales, like the slates on a roof, but of irregular form. These give it a serrated outline at the sides, and when strongly developed, as in wool and some furs, and further raised by chemical treatment, confer the property of felting. Within these scales, which are called the "hair cuticle," is a fibrous substance which forms the body of the hair; and sometimes, but not always, there is also a central and cellular pith, which under the microscope frequently appears black and opaque, from the optical effect of imprisoned air. On boiling or long soaking in water, alcohol, or turpentine

FIG. 12.—Section of goat-skin showing sweat-ducts and sebaceous glands. Unhaired. (×84.) Photograph by R. H. Marriott.

the air-spaces become filled with the liquid, and then appear transparent.

The fibrous part of the hair is made up of long spindle-shaped cells, and contains the pigment which gives the hair its colour.

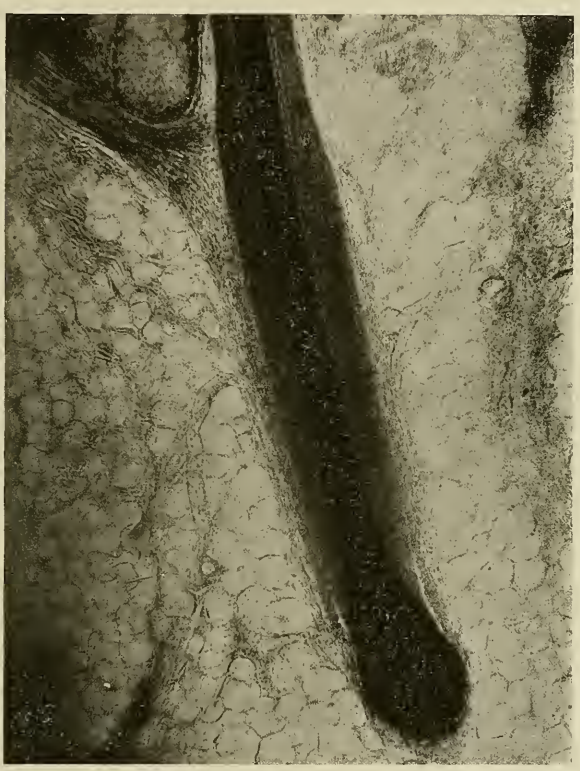

FIG. 13.—Photomicrograph by Mr A. Seymour-Jones of a hair, hair follicle, and the *erector pili* muscle.

The hair may be clearly traced downward to the root bulb and surrounding the hair follicle. The attachment of the erecting muscle (p. 55) is shown on the left side of the hair follicle, starting at the top, and gradually terminating near the root bulb. Its conformation resembles the spreading of the oak tree at its base. Its powerful hold is well defined, and the reader will appreciate, therefrom, its action. The method of attachment to the grain membrane of this muscle is similar to that of the hair follicle. Between the points of attachment the muscle is shown reduced in thickness, but this reduction is not maintained beyond the point shown in the figure—that is, the thickness remains even throughout until it again meets the attaching end, when it spreads out to secure a strong foundation grip.

These cells are easily seen under the microscope if hair or wool is broken up by treatment with moderately strong sulphuric acid. The hair of the deer differs from that of most other animals in being almost wholly formed of polygonal cells, which, in white hairs, are usually filled with air. In all dark hairs both the hair and sheath are strongly pigmented, but the hair is much the more so, and hence the bulb has usually a distinct dark form. The dark-haired portions of a hide from which the hair has been removed by liming still remain coloured by the pigmented cells of the hair-sheaths, which can only be completely removed by bating and scudding.

Just below the grain-layer the ducts of the sebaceous or fat-glands pass into the hair-sheath and secrete an oily matter to lubricate the hair. The glands themselves are formed of large nucleated cells arranged somewhat like a bunch of grapes, the upper and more central ones being highly charged with fatty matter. Their appearance is shown in fig. 14. A good deal of the pasty substance worked out in unhairing (yellow on a white hide) consists of these sebaceous glands, more or less broken down by liming, but still recognisable by the microscope. The base of the hair is a bulb, enclosing the hair papilla *h* (fig. 15), which is a projecting knob of the *corium*, and which by means of the blood-vessels contained in it supplies nourishment to the hair. The hair-bulb is composed of round soft cells, which multiply rapidly by division, and pressing upwards through the hair-sheath become hardened, thus increasing the length of the hair.

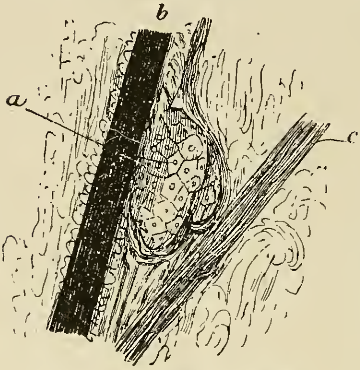

FIG. 14.—*a*, sebaceous gland; *b*, hair; *c*, erector muscle. (× 200.)

The cells outside the bulb, shown at *f* in fig. 15, pass upwards as they grow, and form a coating around the hair, known as the "inner root-sheath."

In the larger text-books of histology a good deal more detail is given of the structure of hair and its sheath, which is omitted here as unimportant for the tanner.

In embryonic development a small knob of cells forms on the under side of the *epidermis*, over a knot of capillary blood-vessels in the *corium*, and enlarges and sinks deeper into the latter, while the root-bulb of the young hair is formed within it, surrounding the capillaries from which it derives nourishment, and which form the hair-papilla, fig. 15. In the renewal of hair in the adult animal the process is very similar. The bulb of the old hair withers and the hair falls out, and in the meantime a thickening takes place in the epidermal coating of the lower part of the sheath, and the young hair is formed below, and usually to one side of the old one, growing into the sheath, and taking the place of the old hair. This is one cause of the difficulty of removing ground-hairs in the process of unhairing, since they are not only short, but deeper seated than the old ones.

The process of development of the sudoriferous or sweat-glands is very similar to that of the hairs. They consist of more or less convoluted tubes surrounded with walls formed of longitudinal fibres of connective tissue of the *corium*, lined with a single layer of large nucleated cells, which secrete the perspiration. The ducts, which are exceedingly narrow, and with walls of nucleated cells like those of the outer hair-sheaths, sometimes open directly through the *epidermis*, but more frequently into the orifice of a hair-sheath, just at the surface of the skin. Each hair is provided with a slanting muscle called the *arrector* or *erector pili* (see fig. 17), which is contracted by cold or fear, and causes the hair to "bristle" or stand on end; by forcing up the attached skin, it produces the effect known as "goose-skin." The muscle, which is of the unstriped or involuntary kind,[1] passes from near the hair-bulb to the *epidermis*, and just under the sebaceous glands, which it compresses when it contracts, thus forcing out the oily matter.

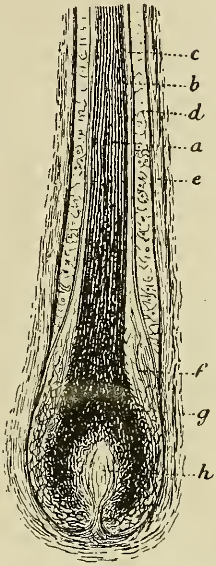

FIG. 15.—*a*, hair; *b*, hair cuticle; *c*, inner root-sheath; *d*, outer root-sheath; *e*, dermic coat of hair-sheath; *f*, origin of inner sheath; *g*, bulb; *h*, hair-papilla.

Beside the hair, and hair-sheaths, and the sebaceous and sudoriferous glands, the *epidermis* layer produces other structures

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[1] The muscles which are under the control of the will, and known as "voluntary muscles," are composed of thin plates, giving them a finely striped appearance under the microscope, while those controlled by the sympathetic nervous system appear simply fibrous. See fig. 21.

of a horny character, including horns, hoofs, claws, and finger-nails; which both chemically and anatomically are analogous to exaggerated hairs, such as the quills of the porcupine. The feathers of birds, and probably the scales of fishes and reptiles, have a similar origin. None of these epidermal structures are soluble in hot water, or capable of producing gelatine or glue. The whole of the hair-sheath and its glands is enclosed in a coating of elastic and connective-tissue fibres, which are supplied with nerves and blood-vessels, and form part of the *corium.*

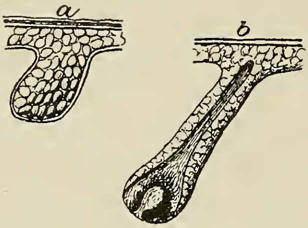

Fig. 16.—Development of young hair.

The *epidermis*, together with the hairs, is separated from the *corium* by an extremely fine membrane or surface called the *hyaline* (hyaline=glassy). This has been the subject of much misconception, for it is so extremely thin that many histologists have doubted even its existence, and have failed to demonstrate it microscopically, and it has been erroneously identified with the upper part of the grain-layer, which, when dry and very thin, as in the "fly-wing" skiver, is almost transparent. Kathreiner believed that he had separated it by accident in the tannery, and the writer had one of his preparations, but it was so transparent that it could scarcely be actually seen under the microscope, though its existence could be inferred by the specks of dirt and broken-down cells which adhered to it. That it has, however, a real existence is proved by its forming the very thin buff-coloured surface of tanned leather, which takes dyes, as well as the colouring matters of the tan differently to the grain immediately beneath it, from which it is evidently distinct. If it gets scraped off mechanically in the beamhouse, or destroyed bacterially in the limes, the exposed portion of the skin remains nearly white instead of colouring, although it has been equally exposed to the tanning liquors. Indeed it is almost impossible to decide by examining the finished leather whether the damage has been done in the beamhouse or after the leather was fully tanned. Seymour-Jones believes that the *hyaline* is always destroyed by the use of strong solutions of alkaline sulphides, but such solutions are sometimes used in the unwooling of cheap glove-leathers, where the preservation of the grain-surface is very important. To avoid misconception, the *hyaline*, if referred to in the following pages, will be called the "grain-surface." Its quantity is so small that it is impossible to study it chemically except upon the skin, and it is not known whether it originates from the *corium* or the *epidermis*. It is possibly identical with the " basal membrane," which can be demonstrated in the hair-bulbs. Seymour-Jones suggests that it is a more or less artificial result of liming, and derived from the bases of the cells of the mucous layer. It is not identical with elastin, since it is not digested by the trypsin ferments. A clear layer of about 0·01 mm. in thickness is very well shown in the puered skin on fig. 42, p. 226, but whether this is really the *hyaline* is uncertain.

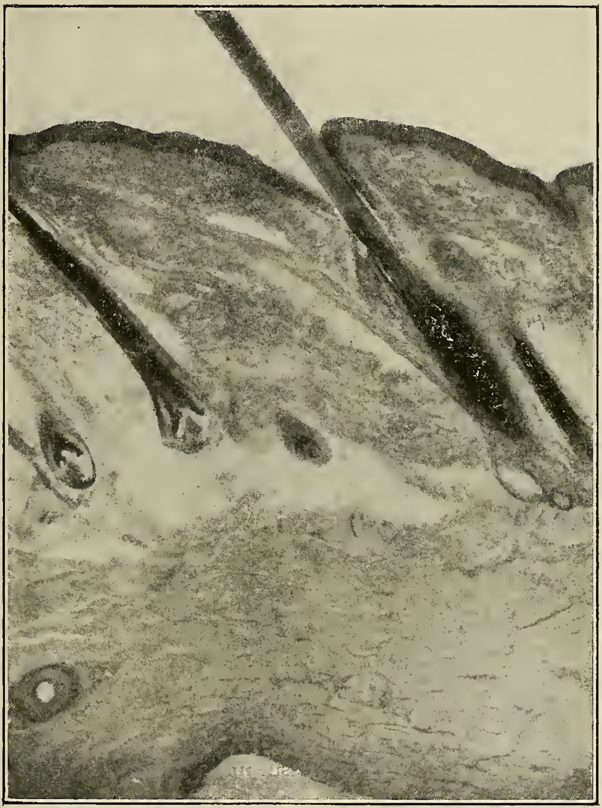

FIG. 17.—Section of calf-skin, showing *arrector pili* muscle and development of hairs. (×80.) Photograph by R. H. Marriott.

The structure of the *corium* is quite different from that of the *epidermis*, which has just been described, as it is principally composed of interlacing bundles of white fibres, of the kind known as " connective tissue " (see fig. 18) ; these are composed of fibrils of extreme fineness, supposed to be cemented together by a substance somewhat more soluble than the fibres themselves. The fibres are not themselves living cells, but are apparently produced by narrow spindle-shaped cells lying against them,

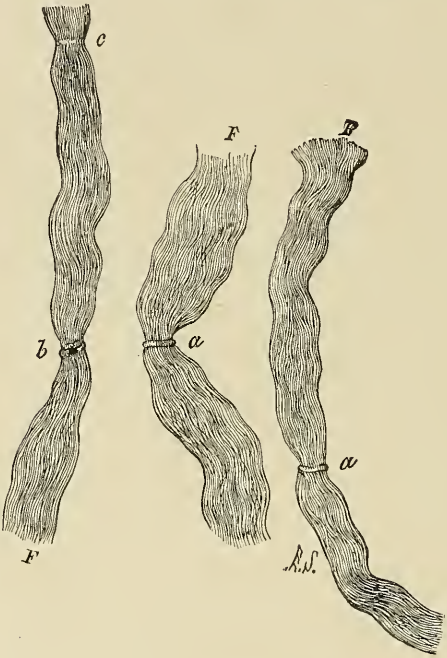

FIG. 18.—Connective-tissue fibres. (Ranvier.)

and possibly travelling up and down the fibre. Rows of somewhat similar cells exist between the fibres of sinews, which are also of connective tissue, though much more compact than that of skin, and in parallel bundles instead of felted together. Interwoven with the white fibres of the grain-layer is a network of the so-called " yellow " or " elastic " fibres. These are chemically very different from the white fibres, which consist of collagen, and when boiled take up water and become converted into glue or gelatines, while the elastic fibres are insoluble in boiling water, and do not appear to combine with tannin. They are also digested by the trypsin ferments, which the white fibres are not, a matter of cardinal importance in the puering process which will be further referred to. The elastic fibres form an actual network, dividing and reuniting, which the white fibres, however interwoven, never seem to do, but always keep their individual identity. When broken, the elastic fibres curl up and contract, and often take spiral forms. They are absent through most of the fibrous part of the *corium*, but become much more abundant as it approaches the flesh.

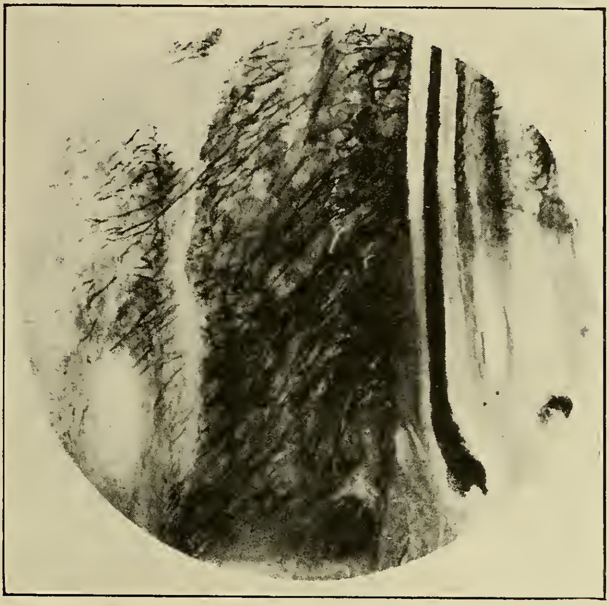

FIG. 19.—Section of ox-hide showing elastic fibres. (×100.)
Photograph by R. H. Marriott.

The outermost layer of the *corium*, which has just been referred to as the "grain-layer," which is just beneath the *epidermis*, is exceedingly close and compact, the fibre-bundles that run into it being separated into their elementary fibrils, which are so interlaced that they can scarcely be recognised. This is the *pars papillaris*, and forms the lighter-coloured layer, called (together with its very fine outer coating) the "grain" of leather. It is just below this part that the sebaceous glands are embedded, while the hair-roots and sweat-glands pass through more deeply into the coarser fibred part below.

The bundles of fibrils are supposed to be held together and the spaces between them filled by some less organised and more soluble substance often called "cement-substance" (Ger. *Kittsubstanz*), of which the nature is unknown, but which seems to be removed by liming. Reimer thought he had separated it, and called it "coriin," but his product was later shown to be merely due to the solution of the hide-fibres themselves. Seymour-Jones (*J.S.L.T.C.*, 1918, p. 36) speaks of the fibre-bundles as being "united by a soft filamentous substance of considerable tenacity and elasticity, known as areolar tissue." This is quite possible, but "areolar tissue" is only a somewhat old name for the looser and more open sort of connective tissue, such as is found below the skin, and surrounds many organs of the body. It was originally supposed to be cellular, as the name implies, but is now known to be merely a network of white connective-tissue fibres like the *corium*, and only contains the flattened and elongated cells which are also found in the skin, and which apparently produce the fibres.

The fibre-bundles in some connective tissues are encircled and tied together by rings or spirals of elastic fibre (see fig. 18), and some histologists have supposed that these were the contracted remains of very thin sheaths of elastin with which the fibre-bundles were originally surrounded, but which have been torn and ruptured by the swelling of the fibrils under the influence of acids or alkalies; and though such sheaths have not been demonstrated, the theory is not altogether improbable.[1] They seem to be absent in most of the fibre-bundles of the skin.

As to the origin of the fibres themselves, they are not living cells with protoplasm and nuclei, and therefore cannot grow by division like the cells of the *epidermis*; but lying between and against the fibres are many flattened and elongated cells which apparently produce the fibres, which may therefore be considered as cell-products rather than actually living tissues. Nothing is known of the origin of the cells, which are possibly modified migratory cells, which latter are probably identical with white blood-corpuscles, lymph- and saliva-cells and the like, and are found not only in the liquid ducts, but wandering through the tissues, which they are able to do from their amœboid character and absence of cell-walls. They apparently play a large and varied part in the animal economy, devouring injurious bacteria and effete substance of all kinds, and conveying it to places where it is required for building up new tissues; and they are supposed to adapt themselves to all sorts of special uses.

The *pars papillaris*, or grain-layer, receives its name from

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[1] Seymour-Jones has spoken of these as "fibre-sarcolemma."

the small projections or *papillæ*, with which its outer surface is studded, and which form the characteristic grain-pattern of the various kinds of skin[1] (see fig. 9), and which contain the nervous ganglia which are the organs of the sense of touch.

The study of the structure of the grain, and especially of the arrangement of the hair-pores, is very important, as it is usually the readiest means of identifying the kind of skin of which a leather is made, which in finished skins with artificially printed grain is often very difficult. (Frontispiece.) The examination is facilitated by wetting and stretching the skin, and by the use of a good lens, or a low power of the microscope.[2]

It has been noted above that the sebaceous glands of the hairs are immediately below the grain-layer, while the hair-bulbs and sweat-glands are somewhat deeper, and frequently associated with large numbers of fat-cells. This is specially the case in sheep-skins, where in both cases the oily matter is so abundant that these regions have been described as distinct layers, and spoken of as " sebaceous " and " adipose " layers. Though it is convenient to retain these names, neither is strictly appropriate, as Lat. *sebum* is *tallow*, while the fatty matter of the glands is mainly a liquid wax, containing no glycerine and much unsaponifiable matter, and in a purified form constituting lanoline, while the contents of the cells of the hair-bulb layer is a soft tallow, glycerides of oleic and stearic acids ; and the term " adipose layer " is objectionable as liable to confusion with the *panniculus adiposus* underlying the *corium*, which also contains large quantities of similar fat-cells. It may be noted that these cells, which are frequent in loose connective tissue throughout the body, are really living cells with nuclei and protoplasm, and the fat cannot be set free and worked out or expressed till the cell-walls are broken down by liming or some other means. They are shown in fig. 20.

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[1] It will be noted that the word " grain " is used by the tanner in at least three different senses, which are productive of much confusion. The extremely thin hyaline forms a natural glaze to the skin, and might well be spoken of as such ; the form and arrangement of the *papillæ* and hair-pores might be called the " pattern " of the grain, leaving the use of the word " grain " or " grain-layer " itself restricted to the *pars papillaris*.

[2] Under the microscope the skin is of course lighted from above by direct light from a window, or by that of a lamp concentrated by a " bulls-eye " condenser. The reversal of the image in the microscope often causes a pseudoscopic effect very puzzling to the beginner, prominences appearing as hollows, and *vice versa*, till the real direction of the lighting is considered.

It has been remarked that both these fatty layers are specially prominent in sheep-skins, and each, when the sebaceous glands and hair-bulbs have been removed at depilation, constitute planes of weakness in the skins. The grain not unfrequently peels at the sebaceous layer, and it is through this that the cut is taken in splitting "fly-wing" skivers, while for ordinary skivers it is through, or just above, the region of the hair-bulbs; and the fatty layer on the surface of the "flesh-split" is removed by skiving before chamoising. In splitting hides in the United States the same loose fatty layer is removed from the flesh-split by a second thin cut, the split being turned flesh side up in the machine, so as to make the substance of even thickness from the flesh surface, which is to be waxed or otherwise finished. In old days, before the splitting machine was invented, grains were frequently torn from the flesh at this point with a little assistance of the hand-knife.

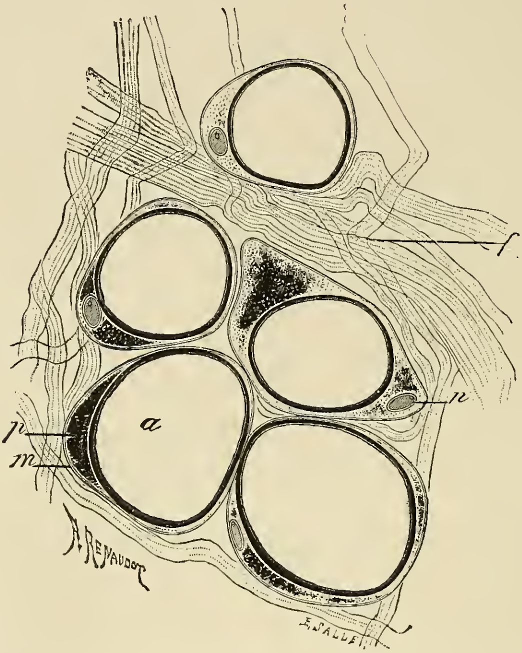

FIG. 20.—Fat-cells in connective tissue. *a*, fat-globule; *p*, protoplasm; *n*, nucleus; *m*, cell-wall. (Ranvier.)

As stated above, the surface of skin which is next to the flesh is firmer than that in the centre, and contains a good deal of elastic fibre, and as the fibres run nearly parallel with the surface, it has a more or less membranous character. The skin is united to the body of the animal by a network of areolar connective tissue (*panniculus adiposus*), which is frequently full of fat-cells, and is then called adipose tissue. This constitutes the whitish layer which is removed, together with portions of actual flesh, in the operation of "fleshing." If a minute portion of adipose tissue be examined microscopically, it will appear to consist of a mere mass of fat-globules entangled in connective tissue. If, however, it be stained with carmine or logwood it may be at once observed that each globule is contained in a cell, of which the nucleated protoplasm, by which the fat was secreted, is pressed closely against the wall (fig. 20).

Many animals (ox, horse, etc.) possess a thin layer of voluntary muscle (red flesh, *panniculus carnosus*) spread over the inner side of the skin, and used for twitching to drive off flies. In rough fleshing this is sometimes left on, and may be a cause of dark flesh in sole leather. Even in the finished leather its striped structure may be detected microscopically (fig. 21).

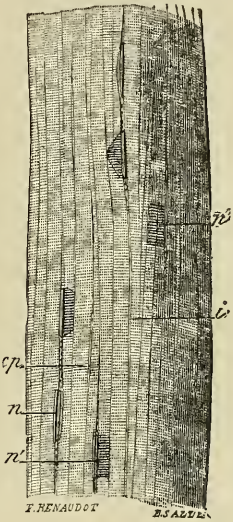

FIG. 21.—Striped, or voluntary muscular fibre. (Ranvier.)

Besides the connective-tissue fibres, the skin contains a varying proportion of fine yellow "elastic" fibres, especially in the grain-layer. If a thin section of hide be soaked for a few minutes in a mixture of equal parts of water, glycerine, and strong acetic acid, and then examined under the microscope, the white connective-tissue fibres become swollen and transparent, (*cp.* pp. 223–227 and figs. 40–43), and the yellow "elastic" fibres may be seen, as they are scarcely affected by the acid. They are, however, much better seen when stained blue with fuchsin and Weigert's stain. The hair-bulbs and sweat- and fat-glands are also rendered distinctly visible by treatment with acid glycerine. On the other hand, the white gelatinous fibres are most easily seen by examining the section in a strong solution of common salt, slightly acidified with acetic acid, or in one of ammonium sulphate; or by staining with some aniline dyes such as safranine. Sections are most readily cut for these purposes by the use of the freezing microtome, or after previous hardening in alcohol. For further details see *L.I.L.B.*, p. 391, and the articles of Seymour-Jones in the *J.S.L.T.C.*, 1917, *et seq.*

Ordinarily in the production of leather only the *corium*, or fibrous part of the skin, is used, and in order to obtain it in a suitable condition for the various tanning processes, the hair or wool, together with the *epidermis*, must be completely removed without damaging the skin itself; and especial care must be taken that the grain-surface or portion next to the *epidermis* does not suffer any injury during the treatment. All the methods employed depend upon the fact that the *epidermis* cells, especially the soft-growing ones next to the *corium*, and those of the *epidermis* layer which surround the hair-roots, are more easily destroyed than the *corium* itself, owing to their different chemical character. The "unhairing" process consists essentially in breaking down these cells by chemical or putrefactive agents, and removing the hair together with the rest of the *epidermis* by mechanical means. Of the various substances which may be used for this purpose lime is one of the most convenient, as its solubility in water is so slight, that a solution of such a strength as rapidly to injure the hide cannot be made, and lime, being divalent, causes only half the swelling of monovalent alkalies. Caustic alkalies, on the other hand, are much more soluble, and unless care be taken to use only the proper quantity, a dangerously strong solution may be made with consequent damage to the skin. The addition of small amounts of sulphides to the lime solution accelerates the unhairing owing to their special solvent action on the *epidermis* structures, and also in the case of alkaline sulphides, by the caustic alkali which is produced by their reaction with the lime. Even if used alone, strong solutions of alkaline sulphides rapidly destroy both hair and *epidermis*, converting them into a mass which may be swept off the skin like wet pulp, and yet they have practically no injurious action on the true skin. Röhm has patented the use of the pancreatic ferments (trypsin, etc.) for unhairing.

In the "sweating" process the *epidermis* cells are broken down by putrefactive organisms and their products, especially the tryptic ferments, so that the hair becomes loose, and may then be either rubbed or scraped off. Ammonia, which is produced during the putrefaction, has also an important solvent action, and its presence doubtless tends to quicken the processes both of unhairing and of destruction.

To obtain useful knowledge of the structure of any particular skin it is not necessary to have a very elaborate or expensive microscope, and it is quite possible to obtain much information merely by the use of a good pocket lens, as, for instance, in the examination of various forms of " grain " and the embossing of one skin to imitate another.

CHAPTER VIII

WATER AS USED IN THE TANNERY

Of all the materials employed in tanning, none is of more indispensable importance than water, and its quality has undoubtedly great influence on tanning, though it is constantly blamed for faults and troubles which are really due to the mistakes of the tanner.

Water is chiefly used in tanneries for soaking and washing hides and skins, for making the limes, the bates, and the tanning liquors, for steam boilers, and in dyeing. For all these purposes it should be as free as possible from impurities, but since water is the most universal solvent in Nature, it is never found pure, but always contains mineral matter derived from the rocks and soil through which it has flowed, as well as organic impurities from decaying animal and vegetable matter. Associated with the latter are usually living organisms of putrefaction (*bacteria*), which may affect the quality of the water for tanning even more seriously than the mineral impurities. The purest natural waters are those which have flowed only over hard sandstones and volcanic rocks, while limestone dissolves freely in the carbonic acid of rain-water. Water sufficiently pure for laboratory use can only be obtained by distillation. The steam-water from heating pipes usually contains large quantities of dissolved iron, and often also volatile organic matters from the oil, etc., which finds its way into the boiler. It may sometimes be made fit for use by boiling (which precipitates the ferrous carbonate present), and subsequent settling or filtration. The use of steam-water containing iron is a frequent source of stains and discolorations in the tannery which more than counterbalances the advantage of its softness.

The " hardness " of natural waters is mostly due to the salts of lime and magnesia which they contain, which precipitate soap in the form of insoluble stearates and oleates, which are useless for washing. It is commonly estimated by determining the amount of a standard alcoholic soap solution which must be added in order to produce a permanent froth on shaking. Theoretically about 12 parts of soap (sodium stearate or oleate) are destroyed by 1 part of calcium carbonate or an equivalent quantity of other lime salts, with formation of insoluble lime soaps (calcium stearate or oleate). Really, the reaction is much more complicated, owing to the dissociation of the soap into free alkali and acid-salts on solution in water. Teed[1] estimates that $\frac{1}{3}$ to $\frac{1}{2}$ more is required than the theoretical quantity, and more in hot water than cold. This uncertainty is partially overcome by testing the soap solution against a known solution of calcium chloride. The presence of magnesia also complicates the test and leads to discrepant results.

The methods of determining hardness originated by Hehner (see *L.I.L.B.*, p. 19, and *L.C.P.B.*, p. 16) are simpler and more accurate than the soap test, and are to be preferred, except for direct determination of the suitability of a water for scouring with soap. "Degrees" of hardness in England are calculated as parts of $CaCO_3$ per 100,000, or sometimes as grains per gallon (70,000 grains). German degrees are parts of CaO in 100,000, and consequently 56 German = 100 English.

Hardness is of two kinds, "temporary" and "permanent"; the former being removed by boiling, while the latter is not so removed.

Temporary hardness consists of the carbonates of alkaline earths held in solution by an excess of carbonic acid. Lime combines with 1 molecule of carbon dioxide to form the ordinary normal carbonate (chalk), which is practically insoluble in water. When, however, excess of carbonic acid is present, hydric calcic carbonate (bicarbonate) which is fairly soluble is produced. This is easily demonstrated by passing carbon dioxide into somewhat diluted lime-water, which at first becomes turbid from precipitated chalk, but soon clears by formation of soluble hydric carbonate. If the solution be now boiled, the hydric carbonate is decomposed, and the excess of carbonic acid is driven off as CO_2, and the chalk again precipitated. The reactions are represented by the following equations :—

$$Ca(OH)_2+CO_2=CaCO_3+OH_2. \qquad (1)$$

$$CaCO_3+CO_2+OH_2=\begin{cases} CaCO_3 \\ H_2CO_3 \end{cases} \qquad (2)$$

Magnesia forms soluble double carbonates in a similar manner, but on continued boiling gradually loses the whole of its carbonic acid, and is precipitated as magnesium hydrate, $Mg(OH)_2$.

One of the most important reactions in connection with temporary hardness is that caused by the addition of calcium hydrate (slaked lime), which forms the basis of Clark's soften-

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[1] *Journ. Soc. Chem. Ind.*, 1889, p. 256. *Cp. also* Allen, *ibid.*, 1888, p. 795.

ing process. When an equivalent amount of lime is added to a solution of hydric calcic carbonate, it displaces the water of the "half-bound" carbonic acid, forming a second molecule of calcium carbonate, which is precipitated together with that originally present, as is represented in the following equation :—

$$\left.\begin{matrix} CaCO_3 \\ H_2CO_3 \end{matrix}\right\} + Ca(OH)_2 = 2CaCO_3 + 2OH_2. \qquad (3)$$

Hydric magnesium carbonate is also precipitated by lime, but the reaction is somewhat different, the magnesia being removed as hydrate as follows :—

$$\left\{\begin{matrix} MgCO_3 \\ H_2CO_3 \end{matrix}\right. + 2Ca(OH)_2 = 2CaCO_3 + 2OH_2 + Mg(OH)_2. \qquad (4)$$

It will be noted that 2 equivalents of lime are required to precipitate 1 of magnesia. Two molecules of sodium hydrate (NaOH) or potassium hydrate (KOH) may be substituted for 1 of $Ca(OH)_2$ with similar results, and in some cases it is practically advantageous to use the former, as the sodium carbonate formed in precipitating the temporary hardness reacts again on the permanent, throwing down the lime and magnesia as carbonates. (See p. 78.)

The use of lime for softening temporary hard waters was originally proposed by Thomas Henry, F.R.S., of Manchester, but was first applied as a practical process by Clark, who, after adding the requisite quantity of lime to the water in a mixing vat, allowed it to stand in a large tank to clear by subsidence, the precipitated carbonate of lime taking from six to twelve hours to settle. The process in its original form is a perfectly satisfactory one, except for the capacious settling tanks which are required, which in some cases are inconvenient and expensive. Messrs Archbutt and Deeley[1] patented a modification of the Clark process, by which the time of subsidence is much shortened, and according to which the precipitated carbonate of lime of previous operations is allowed to remain in the tank, and the fresh charge of water and lime is mixed up with it by means of steam-injectors, which blow in a current of air through perforated pipes at the bottom of the tank, and at the same time very slightly warm the water. The action goes on much more rapidly at a slightly raised temperature than in the cold; and rather curiously, the stirred up precipitate, instead of increasing the time of clearing, settles rapidly and carries down with it that formed in the new operation. The process is particularly suitable for treating waters containing magnesia, from which a

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[1] *Journ. Soc. Chem. Ind.*, 1891, p. 511.

compound of lime and magnesia is apt to be precipitated in a colloid form, which chokes filter-cloths and will not readily settle.

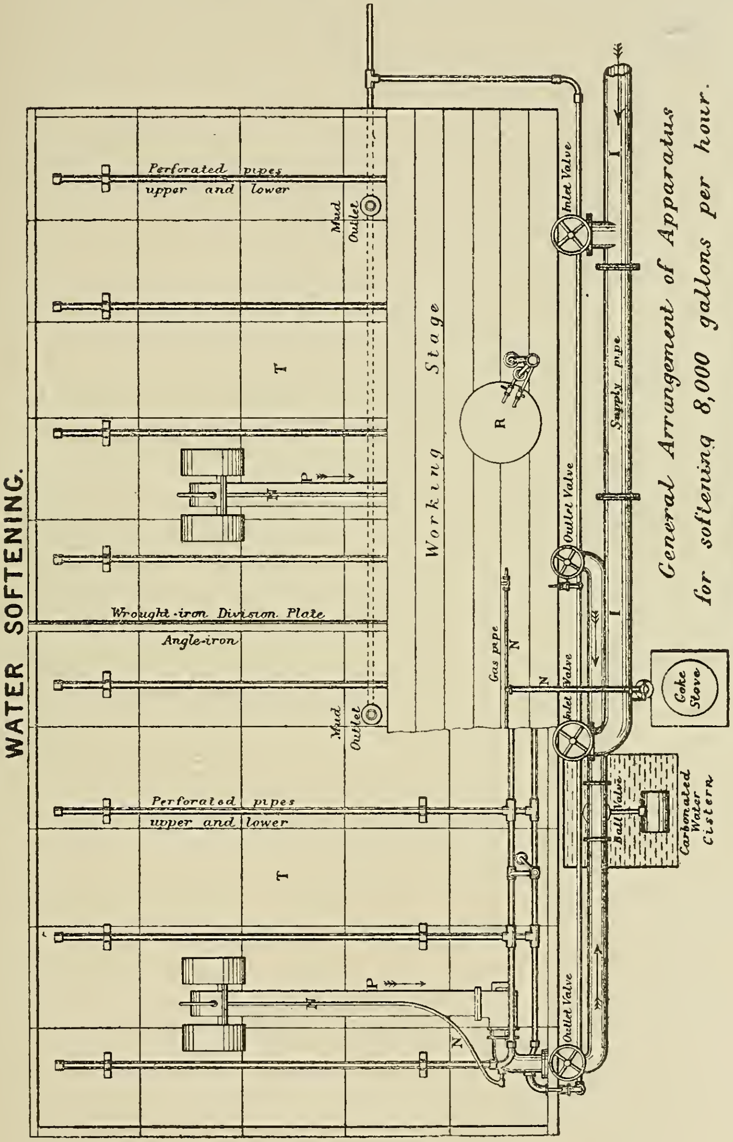

FIG. 22.—Plan of Archbutt and Deeley's Apparatus.

After softening, the water is usually "carbonated" by passing the gases produced by burning coke into the floating exit-pipe through which it falls, in order to retain any remaining traces of carbonates of lime and magnesia in a soluble form, and prevent their subsequent precipitation in the pipes. The apparatus is made by Messrs Mather & Platt of Manchester, and its arrangement is shown in figs. 22 and 23.

Several modifications of the Clark process have been introduced, in which the precipitation is carried on continuously instead of intermittently. The most important of these is the Porter-Clark, in which one portion of the water to be softened flows through an agitator containing excess of lime, with which it forms saturated lime-water, which is passed slowly up a cylinder, where it deposits the excess of suspended lime. The clear lime-water so produced is mixed with a fresh portion of the water to be softened in a second cylinder, also provided with an agitator, the proportion of the two liquids being regulated by cocks. The carbonate of lime is at once precipitated, and is removed by passage through a filter-press. This process has long been in successful operation on a considerable scale at Messrs Hodgsons' tannery at Beverley.

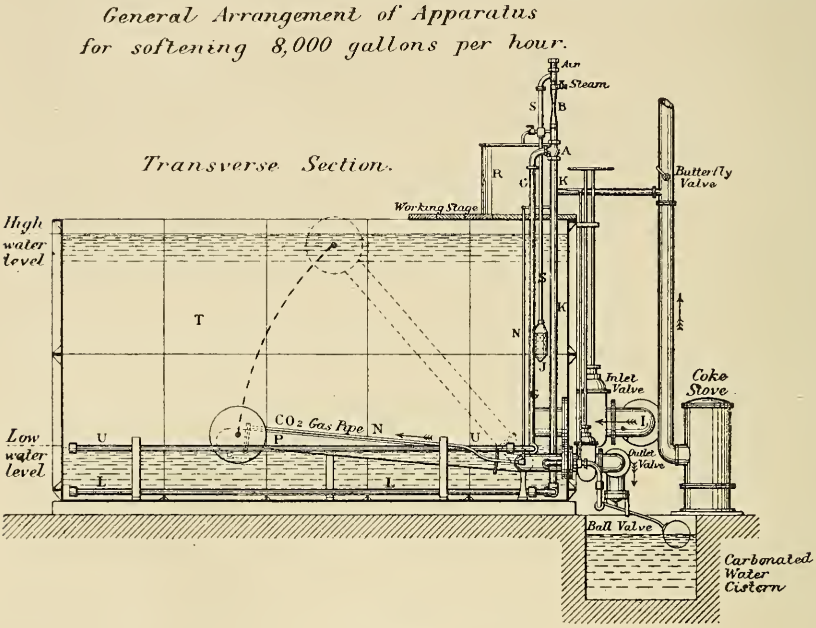

FIG. 23.

Several other forms of filter have also been employed with success, and also methods in which the treated water traverses tanks with sloping partitions, on which the carbonate of lime is deposited. The latter plan was originally patented in France by Gaillet-Huet, and has been introduced into England by Stanhope.

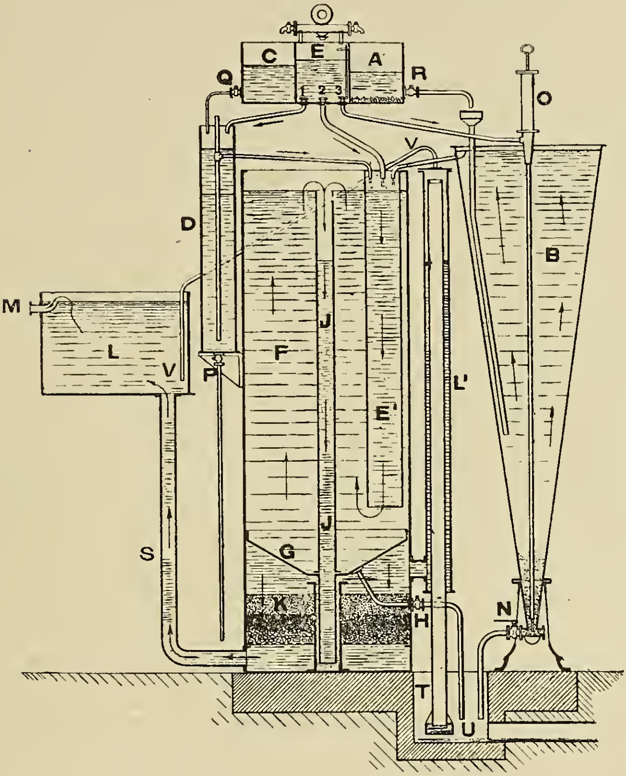

FIG. 24.

A very good automatic apparatus is now made by Messrs Royles Ltd. of Irlam, near Manchester, of which a section is shown in fig. 24.

"In this apparatus the bicarbonate of lime is precipitated by hydrate of lime (lime water), and the sulphate of lime by soda. The softened water is then filtered and discharged. The apparatus acts entirely automatically; all that is necessary is to supply the lime and soda daily, and follow the very simple and clear directions supplied with each apparatus.

"The apparatus consists essentially of an automatic lime saturator and decanter B, a soda chamber D, a water-distributing tank E with a lime-slaking division A and soda-mixing division C, a reaction chamber F, and an automatic self-cleansing filter K.

"The lime saturator B requires no stirring contrivance, and lixiviates the lime completely; and owing to its upward widening shape, it turns the saturated lime water into a clear fluid.

"By a constantly uniform water supply through the micrometer valve 3 from the distributing tank E, which is conducted downwards through the central pipe O, the lime paste at the bottom is stirred up and thoroughly impregnated, and rises, at first partly with the water, until the rapidity of the rising water diminishes so much, owing to the upward widening shape of the saturator, that the undissolved lime particles are no longer able to follow, so that the saturated lime water, clarified, then leaves the saturator B at the top, and is carried into the reaction chamber F by way of the mixing pipe E′.

"Lime dissolves in a definite proportion in water until the latter is saturated. This property renders it possible to continually keep a uniform stream of saturated lime water supplied as required for the precipitation of bicarbonates of lime and magnesia. This uniform addition of lime water is so important that on it substantially depends the degree of purification of the water. Neither in the form of powder nor milk of lime can lime be added in so constantly uniform quantity.

"The soda apparatus D acts in an equally simple and safe manner. Whereas lime dissolves only in a definite proportion, soda is much more soluble. A quantity of soda that will suffice for one or more days is dissolved in the chamber C and let down into D through cock Q. The action of the soda apparatus is based on the fact of the soda solution having a greater specific gravity than water, and thus the water flowing from the distributing tank E through the small micrometer valve 1—which is adjusted in accordance with the amount of soda required—into the soda chamber D, remains always on the surface of the soda solution (no mixing occurs) and displaces the same, it being carried through the small pipe from the bottom upwards, and into the mixing pipe E′, and finally into the reaction chamber F."

Mr E. Munro Payne has patented the use of sodium phosphate for water-softening, and it is no doubt an excellent precipitant for lime, both as temporary and permanent hardness, but its price prevents it taking the place of lime and sodium carbonate on any considerable scale.

A comparatively recent process, called the "Permutit," is of much greater interest, both practically and scientifically. The following details have been kindly furnished by Mr A. Glover of the Research Department of the Wholesale Co-operative Society in Manchester, who has practical experience in its working:—

" In accordance with your request, I take the liberty to send on a few notes on the Permutit process of water softening which I trust will be of use to you. I have arranged the notes under the following heads:—

(1) History.
(2) Composition of Permutit.
(3) Reactions.
(4) Advantages.
(5) Disadvantages.

" (1) In recent time it has been shown that naturally soft waters of certain districts were originally hard, but after percolation through strata containing minerals known as " zeolites " gave soft waters. The " zeolite " is the generic name of a group of hydrated double silicates. The bases found in chemical combination with these silicates are principally magnesium, sodium, calcium, and aluminium. These zeolites exchange bases chemically, but suffer no physical change.

" (2) Hence the application of this idea. Permutit is a patent name of a synthetic compound whose chemical composition may be represented as follows:—

$$2SiO_2, Al_2O_3, Na_2O, 6H_2O.$$

It is a porous material, and appears like ground quartz.

" (3) Assuming Permutit to be represented during the reactions as Na_2Pm, and since Permutit gives only a base exchange during water softening, the following equations will explain the process of water softening:—

$$Ca(HCO_3)_2 + Na_2Pm \rightarrow CaPm + 2NaHCO_3$$

and

$$Mg(HCO_3)_2 + Na_2Pm \rightarrow MgPm + 2NaHCO_3.$$

Hence the temporary hardness is destroyed, and sodium bicarbonate is left in solution. In time the maximum exchange has taken place, and the Permutit becomes inactive. To regenerate the Permutit a 10 per cent. solution of common salt is run into the plant. Regeneration takes place as follows:—

$$CaPm + 2NaCl \rightarrow Na_2Pm + CaCl_2$$

and

$$MgPm + 2NaCl \rightarrow Na_2Pm + MgCl_2.$$

The plant is now washed out, and the hard water supply is turned on as before.

" *Permanent Hardness.*—The following equations indicate the reaction :—

$$Na_2Pm + CaSO_4 \rightarrow CaPm + Na_2SO_4.$$

$$Na_2Pm + MgCl_2 \rightarrow MgPm + 2NaCl.$$

After a time regeneration with common salt solution is necessary.

" (4) *Advantages.*

(*a*) With certain waters it is possible to get zero hardness using this plant.

(*b*) No chemicals to be measured out.

(*c*) No filtration, because no precipitate is produced.

" (5) *Disadvantages.*

(*a*) Production of $NaHCO_3$ for tannery work. This may be harmful.

(*b*) Not applicable for all waters. A water that is too hard will necessitate constant regeneration of the Permutit. A water containing much $MgCl_2$ and $CaCl_2$ will be difficult to control, because

$$Na_2Pm + MgCl_2 \rightarrow MgPm + 2NaCl,$$

also

$$Na_2Pm + CaCl_2 \rightarrow CaPm + 2NaCl.$$

Since common salt is required for regeneration of the Permutit, I think that an equilibrium of the reaction must take place as

$$Na_2Pm + CaCl_2 \rightleftarrows CaPm + 2NaCl.$$

Hence under ordinary working conditions I do not think that all the permanent hardness (*i.e.* $MgCl_2$ and $CaCl_2$), especially if it is high, will be removed.

" Nevertheless, for general commercial purposes I think that it has many useful applications."

So far as is yet known, from the tanner's point of view, it is hardly necessary to make any distinction between lime and magnesia, either or both of which may be considered simply as " hardness." A hard water probably softens dried hides more slowly than a purer water, though it is possible that the observed difference in the time required may be due in many cases to the lower temperature of wells from which hard water is generally derived. In the actual " limes " the hardness of the water can have no appreciable influence, though if sodium sulphide be used alone for unhairing, a certain waste occurs from temporary hardness which may render it advisable to add a little lime. It is in washing the hides free from lime that the influence of hard water is first distinctly felt. If limy goods, after unhairing, are placed in a water with much temporary hardness, the same action occurs as in Clark's water-softening process, and chalk is deposited in the surface of the hides, making them harsh and apt to "frize" or roughen the grain in "scudding." The common, but not wholly satisfactory, expedient is to add a little lime, or better, a few pailfuls of lime liquor, to the water before putting in the hides. The best plan is to use a properly softened water. Permanent hardness is not injurious in this way.

Unfortunately it is not the grain alone which is injured by the use of hard water for washing the hides, but on coming into the liquors the precipitated bases combine with the acids and tannins, forming compounds which oxidise and darken when exposed to the air, and which are the commonest causes of stains and markings on all descriptions of leather. Even when goods are drenched or bated before tanning the injury is not prevented, since the weak organic acids which are capable of removing the lime (as such) from the hide have little effect on the precipitated carbonate, which can only be dissolved by the use of stronger acids. It must be noted that the same injurious effect on limed goods is produced by free carbonic acid, which may be present even in soft waters.

When temporarily hard waters are employed for leaching tanning materials, the carbonic acid is displaced by the tannins, which form compounds similar to those just mentioned, which are incapable of tanning, and darken and discolour when exposed to the air. Though the amount of lime present in a liter of even the hardest water is very small, yet in the aggregate of thousands of gallons used weekly in a good-sized yard it amounts to something very considerable, and as the molecular weight of tannins is very high, the quantity destroyed is many times that of the lime present. This loss can be prevented (*a*) by the addition of sufficient mineral acid to convert the temporary into permanent hardness, (*b*) by the use of oxalic acid, which precipitates the whole of the lime as oxalate, or, (*c*) best of all, by softening the water by suitable treatment before use. Each part of temporary hardness reckoned as $CaCO_3$ (*L.I.L.B.*, p. 19; *L.C.P.B.*, p. 17) requires 1·26 parts of crystallised oxalic acid or 0·98 part of H_2SO_4, or, say, one part of ordinary oil of vitriol of sp. gr. 1·840 per 100,000 parts of water.

As the lime and magnesia of temporarily hard water is thrown down by boiling, it is deposited in steam boilers as a soft precipitate, much of which can be blown out by suitable sludging;

but if oils or fats obtain access to the boiler, a soft, bulky, adherent deposit is formed, keeping the water from the plates, which may become red hot, and lead to collapse or explosion. This effect is not produced by mineral oils, which, on the contrary, tend to prevent adherence of scale to the plates, and as suitable mineral oils are not only cheaper but much less injurious to the working parts of steam engines than animal or vegetable oils or tallow, they should always be used in preference for cylinder purposes.

Water which is temporarily hard owing to calcium and magnesium carbonates is unsuitable for *dyeing*, as the carbonates react with basic dyes, precipitating the colour-base, and so rendering a part of the dye useless. Further, as this precipitate is deposited on the skins it causes uneven dyeing and gives rise to spots and streaks. In dyeing with basic dyes, therefore, it is advisable to add sufficient acetic acid to the water before use to exactly neutralise the carbonates present. Of course this treatment is quite unnecessary when acid dyes are employed, as acid is usually added with the dye, and with dyewoods the presence of a little calcium salt is advantageous.

As each "degree" of total hardness represents a soap-destroying power of at least 2 oz. of soap per 100 gallons of water, allowance must be made in making up "fat-liquors" with soap and oil for the loss of soap due to its precipitation by the mineral matter in the water. The sticky lime-soaps are apt to adhere to the leather and interfere with glazing, so that it is much better to employ a soft water.

Permanent hardness of water is generally caused by sulphates of lime and magnesia, and more rarely by chlorides and nitrates. As none of these can be precipitated by lime, permanent hardness cannot be removed by Clark's process, nor can it produce the injurious effect on limed hides which have been attributed to temporary hardness. Neither can the lime and magnesia present combine with the tannins if used for leaching, since they are already fixed by stronger acids, and at most can only act injuriously by slightly lessening the solubility of the tannins. Even this effect cannot be regarded as proved, though it deserves further investigation.[1] Permanent hardness is therefore of little

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[1] The investigations of Nihoul ("Influence de la nature de l'eau sur l'extraction des matières tannantes," *Bull. de la Bourse aux cuirs de Liège*, September 1901) on the tanning waters of Belgium seemed to show that permanent hardness is more injurious in the extraction of tanning materials than has generally been supposed. If the tannins existed as sodium or potassium salts in liquors very free from acidity, it is quite conceivable

moment as regards the ordinary uses of the tannery, though it has considerable influence in some of the processes of dyeing, and acts very injuriously where soap is used for scouring, as in the washing of sheep-skins for wool mats, since each part of lime reckoned as carbonate destroys at least twelve parts of pure soap (sodium stearate or oleate), producing a sticky and insoluble lime-soap which adheres to the fibre. In sole leather tanning permanent hardness is sometimes advantageous, especially if it be due to calcium and magnesium sulphates, and Vignon recommended that sulphuric acid should be added to the water before use in quantity sufficient to exactly neutralise the carbonates which cause temporary hardness, as magnesium and calcium sulphates are not injurious, but tend to plump the hides. It must be remembered, however, that the carbonic acid liberated may still have prejudicial effects on limed hides.

Permanent hardness is most objectionable in waters employed for boiler-feeding, and calcium sulphate is especially so, as it becomes nearly insoluble in water at 150° C. or 55 lb. steam-pressure, and is deposited on the plates as a hard crystalline scale which must be chipped off with a hammer. Where many boilers have to be worked with a hard water, it is much the most satisfactory to soften the water with caustic soda, or with lime and soda together, before it comes into the boiler, but in cases where the plant required would be too costly, boiler-compositions are sometimes used with good effect, though considerable caution is advisable, since some of them affect the plates injuriously. The active constituent of many boiler-compositions is soda-ash or sodium carbonate, which acts by double decomposition with the calcium sulphate, forming sodium sulphate, and precipitating calcium carbonate as a sediment which is easily washed out. Most tanning materials, and even spent tan liquors, will prevent or lessen incrustation if mixed with the feed water, but sometimes corrode the plates if used too freely. This danger is lessened if they are used in conjunction with soda. Heavy mineral oils, either introduced in small quantity with the feed water, or painted on the sides of the boiler when cleaned, are useful in preventing the formation of a coherent scale.

The removal of permanent hardness from water is easily

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that they might react with calcium sulphate, forming insoluble calcium tannates. Wilson and Kern ("The Non-tannin Enigma," *J.A.L.C.A.*, 1918) have shown that the effect of electrolytes which do not combine with hide-powder is invariably to raise the non-tannins, and so diminish the apparent amount of tannin.

effected in most of the forms of apparatus employed for the softening of water by lime by using a calculated quantity of sodium carbonate in addition. The reaction is represented in the case of calcium sulphate by the following equation:—

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The conversion of magnesium sulphate into carbonate may be similarly effected, but as the latter is somewhat soluble, an additional equivalent of lime must be used to precipitate it as hydrate. Magnesium salts, from their solubility, do not cause scale on boilers (though the chloride is apt to produce corrosion), but they are equally destructive of soap with the calcium salts. Caustic soda will remove temporary hardness, and after becoming converted into carbonate will further react on any permanent hardness present; and its use is therefore sometimes convenient in small softening plants, but it is not more effective, and considerably more costly, than a suitable mixture of lime and sodium carbonate. Even with these, Archbutt states that the cost of softening permanent hardness is about ten times as great as that of removing temporary hardness with lime only.[1]

Beside the method just mentioned, various others are described for the softening of permanent-hard waters (see pp. 71–75).

As regards the influence of other impurities, our knowledge is far from complete, but the following are the most important matters likely to be present:—

Mud under any circumstances is objectionable. It frequently contains organic slime and organisms which encourage the putrefaction of hides placed in it to wash or soften. It also almost invariably contains iron as one of its constituents, and hence stains leather and gives dark-coloured liquors. It is not easily removed by filtration, as large filter-beds are expensive and difficult to keep in order, and much space is required to clear water by subsidence. Some mechanical filter which can be easily cleaned, and used under pressure, offers the best chance of success. The Pulsometer Company make one, consisting of sponge tightly packed below a perforated piston. To cleanse the filter a stream of water is passed the reverse way, and the piston raised and worked up and down, either by hand or power, so as to loosen and knead the sponge. Filter-presses, in which cloths, or in some cases sand, are used as the filtering medium, are also well adapted for the purpose. If a water be softened

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[1] *Proceedings of Inst. of Mech. Engineers*, 1898, pp. 404–54, in which much valuable information on water-softening is given.

by Clark's or other process the precipitated chalk carries down the mud with it, together with most of the organisms.

Iron is always an objectionable impurity in the tannery, though it is less injurious to the quality than the appearance of the leather produced, and indeed German sole leather tanners frequently put old iron in the handlers to darken the colour of the leather, and apparently, if not really, to quicken the tannage. It must not be present in waters used for dyeing. Iron oxide is frequently present as a mud merely, and in this case can be removed by filtration. It is rarely in solution in any other form than that of acid carbonate, since sulphate or chloride could not exist in presence of bicarbonate of lime. In this form, iron is precipitated at once by boiling or on the addition of lime, like the temporary hardness due to other bases, in the form of ferric hydrate, and more slowly by oxidation on exposure to the air. The mud produced by softening waters which contain iron must be completely removed by filtration, or subsidence, before the water is used for leaching, or the iron will redissolve in the acids of the liquors. Iron is not perceptibly injurious in the limes, but in the bates and wash-pits sometimes causes stains, which are scarcely visible till blackened by the tanning liquors. In presence of sulphur (from sulphide of sodium or the decomposition of sulphates by the sulphur-bacteria nearly always present in bates and soaks) the stains become bluish or greenish-black, and a black deposit is frequently produced on the sides of the pit, in which the threads of sulphur-bacteria (*Thiothrix*) can often be recognised by the microscope. As ferric salts not only combine with the tannins, but are themselves tanning agents (see p. 275), they are rapidly absorbed by leather, and iron is always present in leather ash. (For detection and estimation see *L.I.L.B.*, p. 40; *L.C.P.B.*, p. 23.)

Alumina, except as clay, is rarely present in waters, and probably harmless in any water likely to be used in tanning.

Soda is sometimes present in considerable amount, as sulphate, chloride, or carbonate. The sulphate slightly increases plumping in limes. The chloride, if present in material quantities, as in tidal rivers, lessens it, and may cause thin and soft leather, and in large amounts will greatly impede the proper exhaustion of many tanning materials. Sodium carbonate is sometimes present in considerable quantities, as in some of the waters of the Leeds district. It may coexist with temporary hardness, and produces similar injurious effects, but waters in which it is present cannot have any real permanent hardness. It may be neutralised by the very cautious addition of an acid, or by admixture of a permanent-hard water. It tends to increase plumping in the limes, but neutralises the free acids of the tan liquors which are necessary in sole leather tanning.

Copper, lead, and other metallic bases are not likely to be present in any waters used for tanning in quantities sufficient to be injurious.

Sulphuric acid rarely occurs free in water, and then only in such traces as would be harmless for tanning, though possibly injurious to steam boilers. As sulphates it is most common. Alkaline sulphates are not known to have any deleterious action. The sulphates of lime and magnesia are the principal cause of permanent hardness, *q.v.* Iron sulphate is sometimes found in colliery waters, from the oxidation of pyrites.

Nitrates and nitrites in water are usually the result of "previous" sewage contamination, and are only important as an indication of the possible presence of the putrefactive ferments, and are of little moment in waters only used for manufacturing purposes, while they seem to be even useful in promoting the "working" of bran drenches, by supplying the nitrogen required by the ferment.

Chlorine is seldom or never present in water in the free state, but only in the form of chlorides, most frequently that of sodium (common salt), the effect of which has been referred to on p. 79. The action of other chlorides is probably similar as regards the swelling of hide. *Magnesium chloride* is very objectionable as a constituent of boiler-waters, as it liberates hydrochloric acid at high temperatures, and corrodes the plates at the surface of the water. This injury can be prevented by addition of soda.

Carbonic acid has been referred to under temporary hardness. Its presence in the free state is a matter of some importance to the tanner (see p. 191).

Silicic acid in a soluble form is present in some waters in considerable quantity. Such waters are said to harden leather, but of this the writer has no personal experience.

Few accurate researches have been made on the effect of the impurities of water on tanning,[1] and though, from what has already been said, it will be seen that they are not without effect, it is probable that in many cases the water is blamed for troubles which are simply the result of mismanagement, and credited with virtues which are really due to careful and skilful manufacture.

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[1] See Nihoul, *loc. cit.*; also Report of American Commission on "Effect of Hard Water on Tannins," *J.A.L.C.A.*, 1918, p. 409; and Wilson and Kern, *loc. cit.*

The hardness of water, and the dissolved carbonic acid which it contains, are, together with its temperature, the principal factors which determine whether a hide will plump or fall in it. Almost the only careful investigation of this point has been made by W. Eitner.[1] He placed pieces of hide, unhaired by sweating, and quite flat and fallen, in water for four days at a temperature of 46° F. (8° C.) with the following results :—

1.	In distilled water . . .	Scarcely at all plumped.
2.	,, water saturated with CO_2 .	Well plumped.
3.	,, ,, with lime bicarbonate, 20° German scale of hardness	Tolerably plump.
4.	,, ,, ,, magnesia bicarbonate, 20° do.	,, ,,
5.	,, ,, ,, lime sulphate, 20° do. . .	Well plumped.
6.	,, ,, ,, magnesia sulphate, 20° do.	Best plumped.
7.	,, ,, ,, magnesium chloride, 20° do. .	Not at all plumped.
8.	,, ,, ,, common salt, 20° do. . .	,, ,,

(20° German scale equal 36° or parts of $CaCO_3$ per 100,000 ; see p. 67.)

The peculiarities which were shown by the hide pieces on removal from the water were maintained throughout the tanning, which was conducted in imitation of the Austrian method, the hide being swollen and coloured through in weak birch-bark liquors, made with distilled water and acidified in each case with equal quantities of lactic acid, and finally laid away, till tanned, in a mixture of oak bark and valonia. No. 6, from magnesium sulphate, was the best ; then No. 2 ; No. 3 was less good, but all the pieces from 1 to 6 were firm, close, and of good substance and texture, No. 1 having swelled well in the sour liquor. On the other hand, 7 and 8 scarcely swelled in liquor, but remained flat throughout, and were looser, thinner, and of finer fibre. From this experiment it is clear that while sulphates and carbonates exert a favourable influence on plumping, chlorides do the reverse, as they themselves not only do not plump, but they place the hides in an unfavourable condition for the plumping action of acids in the liquors. These experiments are quite borne out by the writer's experience in practice. The water at the Lowlights

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[1] Gerber (1877), iii. p. 183 ; *cp.* also Chap. X.

Tannery, which in dry weather was mostly obtained from beds of what was originally sea-sand, and which consequently contained a very abnormal proportion of chlorides (up to 68 parts NaCl per 100,000), required special and very careful management to make thick leather, notwithstanding the fact that it contained a considerable quantity of calcium and magnesium sulphates. These facts also indicate the importance of the thorough removal of salt from hides intended for sole leather. Plumping is not a desirable thing in leather intended for dressing purposes, and it is possible that the use of a small percentage of salt in the liquors or wash waters might in some cases enable bating to be dispensed with.

There is no practicable means of removing chlorides from water, but Eitner suggests the addition of a small quantity of sulphuric acid to water containing much temporary hardness (bicarbonates), in order to convert it into permanent hardness (sulphates), which, as stated above, plumps better. The amount required may be calculated from an acidimetric determination of temporary hardness (see *L.I.L.B.*, p. 19; *L.C.P.B.*, p. 16). A simple, but not very accurate, guide is to add enough acid to purple, but not to redden litmus paper even after moving the latter about in the water for some minutes. In practice the acid must of course be very thoroughly mixed with the water by stirring and plunging. It must be borne in mind that Eitner's experiment was on sweated hides, and that with limed hide, which is kept plump by the dissolved lime retained in the hide, different results as regards carbonic acid and bicarbonates would be obtained. Both these would convert the lime in the hide into chalk, which is insoluble and inert, and the hide would fall, at any rate when the lime was completely carbonated, while hides would remain plumpest in waters most free from substances capable of neutralising lime. From this we might conclude, what may be *a priori* expected, that the purer the water, the plumper limed hides remain in it, but in soft but peaty waters hides fall rapidly, from the neutralisation of the lime by the weak organic acids of the peat. Such waters are dangerous for domestic use from their solvent action on lead, but this danger can be entirely removed by storing the water in limestone reservoirs, or allowing it to flow slowly through a limestone culvert before use. In some towns in the north of England a small quantity of lime is added so as to neutralise the water as it leaves the reservoir and before it enters the mains.

Wherever the conditions of putrefaction or decaying organic matter are present, as in a bate, hides fall rapidly, and in extreme cases even the presence of the stronger acids will not maintain plumpness. Eitner mentions the case of a stream at Vissoko in

Bosnia, which was in special repute among the tanners from its power of pulling down hides rapidly, and which took its rise in a common on which the pigs of the town were pastured. The causes of this action are no doubt due to the products of putrefaction, but are somewhat obscure. Bacteria present in water are a frequent source of injury in the soaks, and probably in other stages of the tanning process.

Rain water and the water of streams in mountain districts of hard igneous rock are generally nearly free from mineral constituents. This is the case with the Glasgow water from Loch Katrine, and the Thirlmere water which supplies Manchester. Such water, if cold enough, and free from mud and organic impurity, is the best for almost every purpose in the tannery. Most river-water contains material quantities of mineral matter, though it is usually softer than that of springs or wells.

For further details as to the chemical examination of water, and the methods of determining the amounts of its different constituents, see *L.I.L.B.*, pp. 18 *et seq.*, and *L.C.P.B.*, p. 16.

CHAPTER IX

PHYSICAL CHEMISTRY IN APPLICATION TO LEATHER MANUFACTURE

THOUGH all sciences are really parts of one great whole, its immense extent makes it necessary to specialise, and to separate by more or less arbitrary divisions. One of the latest of these is Physical Chemistry, and it is rapidly increasing in both scientific and technical importance, though its limits are not easy to define. While the general chemistry of the past dealt mainly with the properties and reactions of elements and their compounds, and was satisfied to state that under given conditions such and such actions would take place, physical chemistry seeks to find the underlying laws of these changes, and to explain them by mechanical and physical causes which can be exactly and mathematically expressed. In general chemistry the atomic theory, the theory of valency, and the laws of gas and vapour pressures represent the beginnings of physical chemistry, but it now embraces large portions of the kindred sciences of electricity and thermodynamics, and some knowledge of physics is necessary before they can be understood.

As it cannot be assumed that all readers of this work are familiar with these ideas, it is necessary to treat them in an elementary and explanatory way before attempting to apply them to the problems of leather manufacture, a large part of which depend on physical chemistry for their elucidation. Mathematics is as far as possible avoided, and where used is always of the most elementary sort.

Constitution of Matter.—It is one of the fundamental ideas of general chemistry that all compounds are built up of atoms, but modern chemistry has taken a further step, and explains that the atoms themselves are built up of electrons, which are conceived as particles of electricity itself. These electrons are both negative and positive, and it is usually supposed that one or more large positive electrons occupy the centre of the system, with a number of negative electrons grouped round them. This view has been greatly strengthened by the fact that elements like radium give off a constant stream of electrons, and in doing so undergo change themselves, radium itself becoming ultimately converted into a form of lead. The electrons themselves are minute charges of + or − electricity, and of course exert the usual attractions on those of opposite sign, which constitute chemical affinity. Electric currents are, in all probability, streams of free electrons.

States of Matter.—Accepting the ordinary chemical theory, we assume that all matter as we know it is built up of *molecules* consisting of groups of atoms held together by their chemical (electrical) affinities ; and that for any individual substance these molecules are all exactly alike, containing the same number of the same atoms, arranged in the same way. We may now try to form some mechanical conception of matter as we see and feel it in its various forms—solid, liquid, and gaseous. In no case are the molecules at rest, but always in a state of rapid vibratory motion which we call heat, and the higher the temperature the more rapid is the movement of the molecules, and the greater the spaces through which they move. They strike each other, and rebound, and tend to separate, but, on the other hand, they are drawn together by an attraction very similar to, if not identical with, the attraction of gravitation, and very possibly electrical in its origin. This attraction is very powerful when the molecules are closely approached, but, like gravitation, rapidly diminishes with distance. These attractions are opposed by the energy of heat, which thus takes the same part in molecular physics which the energy of planetary motion does in the solar system.

Gases.—In the gaseous or vapour state the spaces between the particles are so great that their attractions are inconsiderable, and if unconfined they would fly off into space, while their blows on the walls of any vessel which contains them are the cause of their pressure. The pressure is thus proportionate to the number of blows per second, and consequently to the number of gas-molecules in a given space, and if we double the density of gas, we therefore double the pressure (Boyle's law). Temperature is, in fact, most accurately measured by the pressure (or its reciprocal, the volume) of a given quantity of gas, each degree Centigrade corresponding to an increase of volume or pressure 1/273 of that at 0° C. or freezing point (Gay Lussac's or Dalton's law). From this law a remarkable consequence follows : at −273° C., if the law holds, a gas would have neither pressure nor volume, or, in other words, the molecules would have none of the motion we know as heat, and hence −273° C. is known as the "absolute zero of temperature." Temperatures measured from this point are generally denoted by T, and it is found that measured in this way many relations are much simplified. It is of course impossible to reach absolute zero, but in liquid hydrogen it is approached within a few degrees.[1]

If different gases are confined together in the same space they will of course take the same temperature, and the molecules of each will exert their pressure on the walls independently of the others, so that the total pressure will be the sum of the "partial" pressures of each of the gases. It can be shown also that each molecule must on the average acquire the same energy of motion, whatever its weight, so that it follows that the heavy molecules must move more slowly than the lighter, and that *all* molecules, whatever their weight, must exert the same pressure, or at constant pressure must occupy the same volume. This is Avogadro's law, and the fact that at a given temperature and pressure there must be the same number of molecules of any gas or vapour in the same space is constantly used to determine the relative "molecular weight" of different substances.

The Liquid State differs from the gaseous in that, though mobile, it can be retained in an open vessel, and can only escape by taking the form of vapour or gas. We may conceive that the molecules of liquids, though still possessing heat-motion, are so much closer together that their attraction is sufficient to prevent their separation, though they can still move within a limited distance. Their motion can indeed be shown indirectly by the constant vibration of small particles, such as bacteria (Brownian motion), which can be seen in the microscope, and which is caused by the bombardment of the liquid molecules.

Vapour-pressure.—Though the average velocity of the molecules is a constant at any given temperature, individual molecules may have their velocity increased or diminished by collision with others, so that a certain proportion, if they reach the surface, may pass through it and take the form of vapour or gas. On

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[1] These laws of perfect gases are mathematically expressed by the equation $pv = \mathrm{RT}$, where p is the pressure, v the volume, T the absolute temperature, and R the "gas-constant," which is the $p \times v$ of a gram-molecule of gas at 1° T and unit pressure, and of course varies with the units used. If pressure is in grams per cm.^{2}, and volume measured in c.c., $\mathrm{R} = 84{,}736$. This equation is only approximately true of actual gases, though very nearly so of hydrogen, and the deviation is only serious as the point of liquefaction is approached, firstly, because the molecules themselves have an actual volume, and, secondly, because they approach each other so closely that their attractions can no longer be neglected. The equation of van der Waals introduces corrections for these, and is approximately true even of the liquid state. It is $\left(p+\frac{a}{v^2}\right)(v-b) = \mathrm{RT}$, a being a constant of attraction, and b the actual volume of the molecules.

the other hand, vapour-molecules, striking the surface, may be entrapped by its attraction and revert to the liquid form. Of course the denser the vapour the larger the number of molecules will be entrapped in this way, while the hotter the liquid the more will escape, and thus a perfectly definite " vapour-pressure " will be established for a temperature at which these numbers are equal, in spite of the fact that it is merely an average, and that individual particles are constantly passing from one state to the other. Such " equilibria " are common enough in daily life, as, for instance, in the comparative steadiness of the birth and death rates in spite of all sorts of interfering causes, and business depends to a large extent on the steadiness of averages. We shall meet with many similar equilibria in the course of our chemical study.

The vapour-pressure depends on temperature only, and is not affected by the presence of other gases or vapours in the space, each gas or vapour having its own partial pressure. If water be introduced into an exhausted flask, the space will become filled with water-vapour at a pressure solely depending on its temperature, and at boiling temperature equal to that of the air outside. If the flask were filled with air at atmospheric pressure before the water was introduced and then sealed, the pressure would be that of the air in addition to that of the water-vapour, and at boiling point might be double that of the outside air, and explosions have been attributed to that cause.

Critical State.—If the liquid and its vapour be gradually heated in a closed vessel, the density of the vapour will increase with its pressure, while that of the liquid will diminish with its heat-expansion, so that a point will be reached when the two are identical, the so-called " critical temperature," above which there is no distinction or separation between liquid and vapour, and no " liquid surface." Above this temperature, liquefaction is therefore impossible, and it was want of knowledge of this which caused failures of all early attempts to liquefy the more " perfect " gases, of which the critical temperature is very low, that of hydrogen being −234·5° C. That of water is +365° C., and its pressure is 200 atmospheres, or about 2940 lb. per square inch.

Boiling Point.—The boiling point of a liquid is reached when its vapour-pressure exceeds that of the air above it and is able to form bubbles in the interior, and it is therefore dependent on the air-pressure. Thus in a vacuum pan water may boil freely at very low temperatures.

Heat of Evaporation.—When a liquid in an open pan over a gas-burner reaches a boil, no length of time will raise its temperature any higher, the whole heat of the burner being expended on the work of evaporation, that is, in overcoming the internal attractions of the liquid, and setting the molecules free as vapour. The quantity of heat consumed in this way is very large; 100 calories (p. 514) are required to raise a kilogramme of water from 0° C. to 100°, but 536 calories to convert it into steam at the same temperature. (A large amount of heat (80 calories) is also consumed in the melting of ice at freezing point.)

Internal Pressure.—From the attractions which have just been mentioned, the interior of a liquid is subject to very heavy pressures, but these are only exerted on things actually forming part of the liquid, that is, really dissolved in it, and not on what is merely dipped into it, which from this point of view is still outside it. For this reason internal pressures cannot be directly measured, but they can be calculated with some accuracy from the heat of evaporation, since Stefan has shown that to bring a particle actually into the surface consumes half the work which is required to set it entirely free in the form of vapour. For boiling ether the internal pressure is 1284 atmospheres, and for water at freezing point 11,000 atmospheres, or about 72 tons per square inch. Though the internal pressure cannot be directly measured, its effects are visible in several ways, as, for instance, in the large force required to tear liquids apart when free from gas-particles, and in the violent "bumping" of boiling gas-free liquids, of which the pressure must rise much above that of the atmosphere before it can form a fresh bubble.

Surface-tension is also a consequence of these forces. Although they are of such great intensity, the attraction rapidly diminishes with distance, and the surface-layer in which they have been partially overcome is only of a thickness to be measured in millionths of a millimeter, while throughout the rest of the liquid they are undiminished. If, therefore, we imagine Stefan's particle actually half out of the surface, it remains attracted by only those particles beside and below it within this very short range, while above it there are only vapour particles beyond its sphere of attraction. By the ordinary mathematical device of the parallelogram of forces we can represent or "resolve" all these attractions into a vertical component pulling directly downwards, and horizontal components of much smaller amount pulling the surface together equally in all directions. These small horizontal components constitute the force known as "surface-tension." In water, in which it is larger than in almost any other liquid, it only amounts to about 75 milligrams across a surface 1 centimeter wide.

Though the force is thus small, its effects are visible in many ways. Certain insects walk on the surface of water as though it were covered by an elastic rubber sheet, and a drop or a bubble will contract and draw back if the pressure within it is lessened. Perhaps its most important effect is that of capillarity. A liquid will rise in a wet tube of small diameter considerably above the level of the surface outside, and in the same way oil is sucked up by a wick, or absorbed by leather or fabric. In a wider tube the liquid is drawn up round the walls, so that the surface is not flat, but takes the well-known meniscus shape. In a vessel which the liquid does not wet, on the other hand, the edges of the liquid are depressed, and the surface is convex, like that of the mercury in a barometer.

Surface-tension may be measured by the extent to which the given liquid will rise in a small tube, but for most purposes the easiest method is that of weighing a given number, say, 100 drops, which are allowed to fall slowly from a small horizontal opening, such as the bottom of a burette. As it is not easy to measure exactly the outside diameter of the dropping tube, it is simplest to make a preliminary experiment with water, of which the surface-tension may be assumed as 75, and calculate that of other liquids measured with the same tube as proportional to the weight of drops as compared with those of the water. The dropping end of the tube should be thin, smooth, and quite free from grease. Very small quantities of some impurities, especially organic, greatly affect the tension.

Much controversy has arisen as to whether the actual surface is a region of increased or diminished pressure, and elaborate theories of tanning, and of colloids generally, have been based on the former assumption, which, in the writer's opinion, is entirely unfounded and unsupported by facts. It need only be said that if the explanation of the causes of surface-tension which have been given here, and which are held by the most eminent authorities on the subject, and especially by van der Waals and his pupils, are correct, the surface is a region not of increased but of diminished pressure and density, and that the actual boundary between the liquid and its vapour is a sort of critical layer where the liquid escaping from the internal pressure is of an equal density with the vapour condensed by the attraction of the liquid surface.[1]

Effect of Dissolved Substances on Surface-tension.—Certain substances, especially salts, increase both the surface-tension and the

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[1] *Cp.* Procter, "The Nature of the Liquid Surface," *J.S.L.T.C.*, 3, 1919, p. 48.

internal pressure. Others, of small surface-tension themselves, naturally lower that of water when dissolved in it, and some organic matters, such as soaps, saponins, etc., reduce it to an extraordinary degree.

Surface-energy is equal to the area of surface × the surface-tension, and it is an important law that it tends to reduce itself to a minimum in every possible way, either by diminishing the surface or reducing the surface-tension. Thus a drop of water falling freely, or of melted lead in a shot-tower, always takes the spherical form, since this possesses the smallest surface in proportion to its volume; and for the same reason, globules of one liquid suspended in another are always spherical. The same law also demands that if two globules of liquid come in actual contact they must coalesce, since the surface of the larger volume is less than that of the two smaller ones. Another consequence is the law of Willard Gibbs, that if a solution contains a constituent which lowers surface-tension this must accumulate in the surface, and this has been shown experimentally to be the case, and is one of the causes of *adsorption,* under which heading it must be further noticed. The same fact introduces a difficulty into the measurement of the surface-tension of impure liquids, since the tension diminishes if the surface stands long enough for the impurity to accumulate in it, and lower results are obtained by the ordinary "statical" methods than by "dynamic" methods, in which the surface is constantly renewed. Some organic matters, especially the saponins, not merely accumulate in the surface, but appear to become coagulated there and form a coherent film.

So far we have considered only liquid surfaces in contact with their own vapour, or with inert gases the influence of which may generally be disregarded, but classes of surfaces (or, more strictly, interfaces) very important for technical purposes are those in which one liquid is in contact with another immiscible with it, or with a solid. Petrol or ether upon water, or water upon chloroform, are instances of the first case, while any solid immersed in a liquid presents the second. If a little petrol be poured on water in a test-tube it will be noted that the meniscus between them still exists, but is flatter than that on the surface of either in contact with air. The reason is that a portion of the attraction of one liquid is exerted on the other and thus partially compensated, and the surface-tension of both is lessened, that of the lesser becoming actually minus, and the tension of the interface is merely the difference between them. This rule is borne out by experiment if it is remembered that practically all liquids have some mutual solubility, and that the liquids actually in contact are therefore the saturated solutions of each in the other, and not the pure liquids themselves.

It has been mentioned that when a liquid of higher surface-tension is in contact with one of lower, the surface-tension of the latter becomes a negative quantity—that is, that the surface tends to spread instead of to contract. It thus follows that one liquid should always spread on another, and it is necessary to explain some apparent exceptions. When an oil in any quantity is poured on water, it often forms drops instead of spreading further. The cause is that the whole surface of the water very rapidly becomes coated with an extremely thin and invisible film of oil, on which the remaining oil has no further tendency to spread. The same is true of solid surfaces, which have presumably a very high though non-measurable tension. It has been shown that water will always spread on a really clean solid surface, but the least trace of grease will prevent it.

There is still the further, and probably very important, case of three liquids of different tensions, or two liquids and a solid. In this case the liquid of lowest tension, tending to spread on the surfaces of both the others, will spread between them, or at least attach itself to both surfaces when exposed, and so form an intermediate film. It is very probable that this explains the use of water in stuffing leather, and is not unimportant in the formation of emulsions.

Emulsions are intimate mixtures of two liquids which are not mutually soluble, such as oil and water. If oil be shaken with water it is broken into small globules, which remain suspended for a time, but ultimately float up to the surface, and again coalesce to a liquid layer. If the globules are extremely small this takes place very slowly, owing to the small effect of gravity and the friction which the particles experience in passing through the water; and possibly also because they may take similar electric charges which cause mutual repulsion. The addition of viscous substances, such as gum or starch, renders such emulsions more permanent by increasing the liquid friction; and even finely divided powders may have a similar effect by coating the globules and preventing their coalescence. (See p. 472.)

The less the difference in the surface-tensions of the two liquids the more readily such emulsions are formed, and if therefore a third substance, such as soap or saponin, which lowers surface-tension and often forms surface-films, is added, it greatly facilitates the operation and conduces to the permanence of the emulsion. Small quantities of alkali have a similar effect on oils, saponifying the traces of free fatty acids which are always present. It is highly probable that these third substances act also by coating the globules when formed, as has been explained in the preceding paragraph, and so preventing their coalescence, and rendering the emulsion permanent. The bearing of these facts in the preparation of fat-liquors is obvious. Some oils are much more readily emulsifiable than others, especially if they contain free fatty acids or some oxidised fats, as is the case with sod oil and degras. Addition of a trace of oleic acid to a neutral oil is often useful. Sulphonated oils are also very powerful emulsifying agents. The author has examined a sample of mineral oil containing at most 20 per cent. of sulphonated oil which emulsified spontaneously to a milky liquid when poured into water. Sulphonated and oxidised oils all contain traces of water-soluble substances which probably play the part of the intermediate coating substance.

It must not be forgotten that in any emulsion of two liquids either may form the separate globules or " disperse phase."

Solution.—Emulsions or suspensions of solids may be so finely divided as to possess most of the properties of solutions, and will be considered later under the head of *Colloids*, but true solutions may be regarded as mixtures so intimate that the individual molecules of the dissolved body come within the sphere of attraction of those of the solvent, and take part in its internal pressure, thus forming a single homogeneous liquid.

Many liquids will mix or dissolve in each other in any proportions, *e.g.* water and alcohol ; the attraction of the alcohol for the water-molecule being as great or greater than that of alcohol for alcohol, or water for water. In other cases, such as water and oil, or water and petroleum spirit, practically no mixture takes place, their mutual attraction being small ; and each retains a considerable surface-tension at the points of contact, though less than that of the free surfaces, since each exerts an attraction on the other. There are also many intermediate cases, such as water with chloroform, carbolic acid, or ether, in which each solvent dissolves a portion of the other, but the two solutions do not mix, but form separate layers. In these cases an equilibrium is attained, in which there is just as much tendency for either of the liquids to pass into as out of the other layer. In this there is an extraordinary resemblance to what has been said of vapour-pressures ; and the tendency to pass into solution is often called solution-pressure ; and it may be noted that when equilibrium has been reached, not only is the solution-pressure but the vapour-pressure of each constituent equal in both solutions.

Like vapour-pressures, the solution-pressures usually increase with rise of temperature, more of each constituent passing into the other, till at last the composition of the two layers becomes identical, their surface-tensions disappear, and complete mixture takes place. With phenol (carbolic acid) and water this takes place at about 70° C. The similarity of this to the miscibility of liquid and vapour at the critical temperature is very striking, and the point where complete mixture occurs has been called the critical temperature of the two solutions. In these liquid mixtures either body may be considered as the solvent, or the dissolved substance. The distinction is quite arbitrary, but usually that present in largest quantity is called the solvent.

Distribution between two Solvents.—If a substance is soluble in both of two immiscible solvents, it will be distributed between them in a constant ratio, according to its solubility in each, whatever its quantity, and this ratio is generally called the "partition constant." The point is important in the separation of substances by "shaking out," as, for instance, the extraction of tannin from aqueous solution by acetic ether, as it enables us to predict what quantity will be removed by successive shakings.

If, as sometimes happens, the "molecular complexity" is different in the two liquids, as in the case of acetic acid, where the molecules are twice as large in benzene as in water, the ratio of concentration, instead of being simply C_a/C_b, as in the first case, will be $C_a/C_b^{\frac{1}{n}}$, in which the fractional power $\frac{1}{n}$ will be that of the relation of the two molecular weights; thus for the case mentioned it will be $C_W/C_B^{\frac{1}{2}}$, or C_W^2/C_B, where W is the water and B the benzene solution. This case is perhaps not of much consequence to the tannery chemist, but is mentioned because of its analogy to what is called the "adsorption formula."[1]

Adsorption.—If finely divided charcoal, or many other fine powders, be shaken up with dilute solutions, they will in many cases, dependent on the nature of the dissolved substance, fix a portion on their surface much larger than its concentration in the liquid, and larger in proportion in dilute than in more concentrated solutions. Thus bone-charcoal is constantly used to decolorise sugar solutions, and charcoal will also remove considerable quantities of tannin from aqueous solution. The proportion removed can generally be stated by a formula of the

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[1] The divisor in a fractional power is a "root"; thus $C^{\frac{1}{2}}$ is the square root of C, or $\sqrt{C}$. $C^{\frac{2}{3}}$ is the cube-root of C squared, and so on.

form $\frac{x}{m}=\alpha C^{\frac{1}{n}}$,[1] where x is the weight of substance absorbed, m that of the absorbent, α a constant varying with the substance, C the concentration of the solution, and $\frac{1}{n}$ a fractional index, often about $\frac{1}{2}$, also varying with the dissolved substance.

It has been shown by Willard Gibbs, that any substance which lowers the surface-tension must necessarily accumulate in the surface; and experiments with froth, and other liquid-air or liquid-vapour surfaces, have confirmed his theoretical conclusion. It has been constantly assumed by colloid chemists that the same reasoning must apply to the contact of liquids with solids, but this is by no means obvious, since in such cases the liquid surface has a negative tension, and tends to spread on the solid. For a full discussion of the theory of adsorption, see Freundlich's "*Kapillarchemie*" and other books on colloid chemistry.

Most of what has been said about liquid solutions is also true of solutions of those solids known as "crystalloids."

Solution of Solids.—Matter exists in two states known as "crystalloid" and "colloid." The colloid state is amorphous, and in solution has no definite point of saturation, and in most (probably in all) cases its particles are larger than single molecules, and are often known to be aggregates; and its solutions are emulsions or suspensions rather than true solutions. It is, however, of such importance in leather manufacture, that it will be dealt with in a separate and later chapter, since most of the materials of leather manufacture exist in the colloid state.

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[1] This formula has received no theoretical explanation, and probably has none. It is applicable to a great variety of chemical reactions, which proceed rapidly at first, and gradually decrease. It is frequently called the "adsorption-isotherm," which itself is a misnomer, as an isotherm is a curve of equal *temperature*, yet many people seem to think that because the course of a reaction can be approximately represented by the formula it is a proof that the reaction is physical and not chemical, and may be classed as a surface-phenomenon, a conclusion by no means justified, since it will approximately represent many which are obviously chemical. It is a mathematical consequence of the form of the formula, that if, instead of plotting $\frac{x}{m}$ and $\alpha C^{\frac{1}{n}}$ we plot their logarithms, the result will be a straight line inclined to the axis at the angle represented by $\frac{1}{n}$. This is rarely the case in actual adsorption experiments, the line being almost invariably more or less curved. (It must not be forgotten in plotting negative logarithms, that in the tables, only the index is negative, while the mantissa remains +, and to get the true negative logarithm must be subtracted from the index.)

Solids in the crystalloid state are characterised by regular crystalline form, indicating that the attractive forces of their molecules are exerted in definite directions, giving them a tendency to attach themselves together in regular geometrical arrangements. They themselves dissolve no part of the solvent (though sometimes a definite number of molecules of the solvent combine in forming the crystal, as " water of crystallisation "), but are dissolved by it till an equilibrium is reached in which the tendency of further particles of the solid to pass into the solvent is balanced by that of those already dissolved to attach themselves to the remaining solid, or " crystallise out." Such a solution is " saturated " with respect to the solid residue, but the word has no meaning unless some second immiscible phase, such as solid crystals, is present, and where a body has, as sometimes happens, more than one crystalline form, a solution may be saturated with regard to one of them, and more or less than saturated with regard to another. In " supersaturated " solutions, crystallisation is at once started by the addition of a " seed " crystal of the proper form. This is well seen by dissolving sodium sulphate or thiosulphate in boiling water, and allowing the solution to cool in a flask plugged with cotton-wool to exclude dust. If the minutest crystal of the solid salt is now dropped in, the whole immediately solidifies with evolution of heat.

If a crystalloid substance, such, for instance, as copper sulphate, be placed in a solvent (*e.g.* water), the dissolved salt will gradually spread itself through the whole body of the solvent, though in the complete absence of currents in the liquid the motion is extremely slow, and years may be taken for the diffusion to rise through a few feet. In many cases salts diffuse through aqueous jellies at nearly the same speed as they would through still water. Colloid substances, on the other hand, have little or no power of diffusion, and mostly cannot pass through jellies at all. This is the reason why tannage with mineral salts is so much more rapid than with vegetable tannins, which are of colloid character, and which diffuse through the gelatinous fibres of the hide with extreme slowness.

Osmotic Pressure.—All dissolved crystalloids do not pass through gelatinous membranes with equal ease, and substances are known, mostly gelatinous precipitates, which do not permit the diffusion of many dissolved salts, though they allow water to pass freely. Thin layers of such precipitates form what are called " semipermeable membranes." The existence of such membranes affords us the possibility of direct measurement of the tendency to diffusion, or, as it is generally called, the "osmotic"[1] pressure of dissolved bodies. Thus a porous earthenware battery-cell may be immersed in a solution of copper sulphate, and filled with one of potassium ferrocyanide. In this way its pores will be filled with a gelatinous precipitate of copper ferrocyanide, which is pervious to water, but impervious to most dissolved substances. If now the cell be filled with a dilute solution of some crystalloid, say sugar, and its top closed by a perforated cork fitted with a vertical tube, and the cell be placed in water, the latter will pass into the cell, and the dilute solution will rise in the tube to a height of many feet above the water outside. By substituting a mercury pressure-gauge for the vertical tube exact measures of the pressure in the cell can be made, which is the osmotic pressure of the dissolved substance. At first sight it is paradoxical that water should flow into the solution, apparently against a heavy pressure, but the explanation is simple. Mention has already been made of the enormous internal pressures of liquids produced by the attractions of their molecules. In the solution a portion of this is borne by the osmotic pressure of the dissolved substance, and the water flows in from the outside till an internal mechanical pressure is produced equal in amount to this osmotic pressure. The resemblance of the phenomena of solution to those of vapour-pressure is very obvious, and it is found to be even quantitative, since the measured osmotic pressures are exactly equal in amount to those which the dissolved body would produce if it were in the state of vapour at the same temperature and occupying the same volume as the solution. It acts, in fact, precisely as the "partial pressure" of a vapour. There are several indirect ways of measuring the osmotic pressure of dissolved bodies, as, for instance, from the lowering of the freezing point, or the raising of the boiling point of the solution as compared to those of the pure solvent, which are easier of execution and generally more exact than the direct measurements, and show that in a given volume at the same temperature the same number of molecules will produce the same osmotic pressure whatever their nature, or conversely, that at the same osmotic pressure and temperature equal volumes of any solution must contain the same number of molecules. The use of these facts in determining molecular weight is obvious.

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[1] Solution-pressure and osmotic pressure are really two names for the same force when the solid is present in the solution; the former being employed to signify the tendency of a solid to dissolve, and the latter the pressure produced by the dissolved body which tends to prevent further solution. Thus, in a saturated solution in contact with its solid, the two pressures are always equal, but exerted in opposite directions.

Electrolysis.—Many liquids do not conduct electricity, and *pure* water only does so to a very limited extent, but many solutions conduct freely. The substances which do so in solution are called "electrolytes." The conduction is of quite a different character to that in a metallic wire, which undergoes no permanent change in the process, while that of the electrolyte is always accompanied by chemical decomposition, and the actual transference of matter from one pole or "electrode" to the other. If, for instance, the solution is one of silver nitrate, a certain quantity of electricity will be required to deposit a gram-equivalent of silver on the kathode or, as it is generally termed, the "negative" pole, while an equivalent of nitric acid (or more strictly of NO_3) will be liberated at the anode or "positive" pole. If the same current passes through a solution of copper sulphate, it will also liberate an equivalent of copper or $\frac{1}{2}$ a gram-atom at the kathode and an equivalent of SO_4 at the anode, and through acidified water it will liberate 1 gram-atom of hydrogen at the kathode and the equivalent $\frac{1}{2}$ gram-atom of oxygen at the anode. This quantity of electricity, which is a perfectly definite one, is called a "Faraday" or "farad," after the discoverer of the law.[1]

Ionisation.—A curious apparent deviation from the law of osmotic pressure is noticed in solutions of salts, acids, and alkalies, and indeed of electrolytes generally; thus a dilute solution of sodium chloride produces an osmotic pressure nearly double that corresponding to the number of molecules of NaCl present, and in fact behaves as if it were a solution of Na and Cl existing separately. Such a solution conducts a current of electricity very readily, while at the same time the chlorine is carried to the anode and the sodium to the kathode, where they separate as ordinary molecules of Na_2 and Cl_2 (the Na decomposing the water present and forming NaOH). In fact, the modern theory of electrolysis asserts that these dissociated atoms are not separated from each other by electricity, but that they exist already separated in the solution of the electrolyte, and merely act as carriers for the electricity, and that the work done by the latter is not that of breaking up the salt-molecule, but of giving its dissociated atoms charges of electricity which enable them to combine as new molecules and escape from the electrolyte. Com-

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[1] It is better to avoid the terms "positive" and "negative" and substitute "anode" and "kathode," as the pole connected with the positive of the battery is really the negative of the decomposition-cell, and, as will be seen below, the electric current is probably a flow of negative electrons passing into the kathode, and out of the anode.

plex salts do not always break up into single atoms; thus calcium sulphate dissociates into Ca and SO_4, hydrogen sulphate (sulphuric acid) into 2H and SO_4, and so on. These dissociated atoms and atom-groups are called "ions," and may be monovalent, divalent, or polyvalent, carrying electrical quantities or charges in proportion to their valency. Without discussing the ultimate nature of electricity itself, the matter is most easily pictured by assuming that the molecule of the undissolved salt is made up of an ion with a + charge ("kation," *e.g.* Na) and an ion with a — charge ("anion," *e.g.* Cl), by the electrical attraction of which charges they are held together. In the ionising solution these attractions are balanced by those of other ions, and perhaps by those of the solvent itself, so that they can wander freely *within* the liquid, but in order to take the molecular form of free elements and escape, say as Na_2 and Cl_2, the pair of kations must go to the — pole or "kathode" and give up one + charge, and at the same time a pair of anions must go to the + pole or "anode" and receive a + charge. Thus the Na and all other kations separate at the kathode, and the Cl and all other anions at the anode. The more modern view is that the kations are positive because they are short of a negative (—) electron, and the anions negative because they have one in excess; the galvanic current being therefore a stream of — electrons, flowing in at the kathode, and passing out at the anode to combine with positive ions.

From what has been said, it will be obvious that free ions can only exist in solution, and can neither evaporate nor separate as solids; but that in the liquid they act much like other dissolved molecules, exerting their own osmotic pressure independently of each other or of the dissolved salt, but with the limitation that the solution must always contain equal numbers of + and — ions.

Electrolytes vary much in their tendency to ionise, and even the best of them are only completely ionised in infinitely dilute solutions, but the ionisation always increases with dilution. Just as we have spoken of solution-pressure, we may also speak of ionisation-pressure, since the ionisation is also an equilibrium determined by the point at which as many molecules break up into ions as those which recombine, and if the ionic concentration exceeds this point, ions recombine till the equilibrium is restored. This point has been determined for a large number of substances, and is called the "ionisation-constant." "Strong" acids and bases are those in which it is large, "weak" ones those in which it is very small. Thus for acetic acid it is only 0·000018, that is, acetic acid is only half ionised at 0·000036 normal, while a "strong" acid like hydrochloric or sulphuric is largely ionised even at normal concentration. Ammonia is about as weak a base as acetic is an acid, while soda, potash, and lime are strong. The salts however, even of weak acids and bases, are largely ionised.[1]

The following table gives the ionisation-constants of various weak acids and bases at 25° C.:—

Ammonia	$k=0{\cdot}000023$
Acetic acid	$k=0{\cdot}000018$
Lactic acid	$k=0{\cdot}000138$
Formic acid	$k=0.000214$
Gallic acid	$k=0{\cdot}00004$
Boracic acid	$k=0{\cdot}00000001$
Carbonic acid	$k=0{\cdot}0000003$
Butyric acid	$k=0{\cdot}0000115$
Oxalic acid	$k=0{\cdot}001$

The Mass-law.—It has been known from the earliest times that a "strong" acid would decompose the salt of a "weak" one, setting free the latter, but the cause of this was ill understood, and was attributed to a greater affinity for the base. It is now known to depend simply on the quantity or concentration of the ions, between which, and not with the unionised acids and bases, most chemical reactions take place. In a mixture of equal parts of normal hydrochloric and acetic acids the molecular quantities of each acid will be the same, but for every free acet-ion there will be many thousand chlor-ions, and consequently the chances of meeting an ion of base, if any be present, will be many thousand to one in favour of the chlor-ions. Similarly, if hydrochloric acid be added to a solution of sodium acetate, acetic acid will be set free, but, instead of remaining in the ionised state, it will at once combine with H ions to form the scarcely ionised acetic acid, still leaving the Cl ions in enormous excess, and allowing more acetic acid to be liberated, till its place has practically been entirely taken by the hydrochloric. A point more difficult to explain, but of great practical importance, is that the neutral salt of a weak acid added to the solution of the acid

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[1] The ionisation-constants are generally determined by their electric conductivity at various concentrations as compared to that at infinite dilution, as the electric conductivity varies with the degree of ionisation. Ostwald's dilution-formula gives the ionisation of weak acids and bases as varied by dilution, but does not apply accurately to strong ones. If k is the ionisation constant, v the volume of dilution, and m the proportion of ionised acid to the whole, $\frac{m^2}{(1-m)}v=k$. This formula is of wide use in calculations. The ionisation-constant is numerically half the concentration at which the substance is half-ionised.

weakens it still further. The salt, say sodium acetate, ionises much more freely than the acid, yielding sodium-ions and acet-ions, and the latter, added to those from the acetic acid, increases the acet-ion concentration beyond the very low ionising pressure of acetic acid, and compels the acet-ions to recombine to unionised acid. Thus by adding sodium acetate to acetic acid, or ammonium chloride or sulphate to ammonia, we can reduce their active acidity or alkalinity to any desired degree without lessening their power of combining with and neutralising bases or acids. This has many uses in leather manufacture; thus in deliming with an acid, we can sufficiently reduce its activity to prevent swelling; and in Stiasny's method of "neutralising" chrome leather, the alkalinity of ammonia is so reduced by the presence of ammonium sulphate, that it is impossible to carry the neutralisation too far. The presence of neutral salts of strong acids and bases has, however, little effect in reducing the activity of the stronger acids and bases.[1]

As the difference between the "strength" of an acid or alkali and its combining power for bases (or acids), which is what is determined by titration, may still not be quite clear to the reader, and as it is one of the greatest importance in leather manufacture, it may be well to give yet another illustration from practice. The normal solution of *any* acid (1 eq. per liter) will neutralise and combine with an equal quantity of the normal solution of any base, but may be very different in sourness or apparent alkalinity, as these properties are due to the free ions of H^+ and OH' which are liberated at the same time as the acid or basic ions, and it is the H and OH ions which cause the swelling of hide. Lime and caustic soda are almost equally strong alkalies, but we can safely put a barrowful of lime into a lime-pit, while the same quantity of caustic soda would dissolve the hides. We all know why this is; but little of the lime dissolves, and most remains at the bottom of the pit, and goes gradually into solution to strengthen the liquor as it is taken up by the hides. Almost the same explanation, with a difference, applies to hydrochloric and acetic acids, though both apparently dissolve at once. The hydrochloric acid suffers almost completely the sort of super-

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[1] The mathematical statement is that if a and b are the two ions of which a salt (or acid or base) c is composed, and k is its ionisation-constant, $a \times b = kc$, from which it is obvious that the increase of *either* of the two ions must increase the concentration of the unionised c, as k is a constant. A simple illustration is that a party of either girls or men coming to a dance will increase the number of dancing couples (combined molecules!) by taking partners from those "sitting out." Acids are salts of hydrogen with an acid-ion; alkalies, salts of hydroxyl (OH) with a base.

solution which we call ionisation, and exerts its full strength immediately, while the acetic acid, like the lime, remains in the liquor mostly in an inactive unionised state, and only ionises when the already ionised part has been consumed by the hide.

As the actual ionic concentration is the important point in many technical processes, and cannot be determined by titration, but only by electrometric measurement, or the gradual change of colour of indicators (*cp.* p. 103), it will be convenient to speak of it as the "true" acidity or alkalinity of a solution, as distinct from that shown by titration.

A very interesting example of equilibria is given by an ordinary method of preparing pure common salt. Hydrochloric acid is even more highly ionised than salt, so that if the concentrated acid is added to a saturated salt solution a part of the salt is precipitated. In a saturated solution of sodium chloride with solid salt present we have dissolved salt at the solution-pressure of the crystallised salt, and Na and Cl ions at the dissociation-pressure of the saturated salt solution, and neither affect the others. If we now add hydrochloric acid, it has no effect directly on the solubility of the *salt*, but as HCl dissociates largely into H and Cl, it increases the pressure of the Cl ions, and so compels the salt to recombine till the Cl pressure is reduced to its normal amount. This increases the concentration of the undissociated salt solution, and thus salt is precipitated or crystallises out till the solution is no longer supersaturated with respect to the salt-crystals.

The neutralisation of acids by alkalies in solution is really the combination of the H and OH ions to form water, and hence the heat of the reaction is practically the same for *all* acids and alkalies. The saltions remain ionised, and only actually combine when the solution is concentrated.

Salt-hydrolysis.—Water ionises to a very minute extent into H^+ and OH', only about 0·1 grm. per ton being ionised, and its ionisation-constant is $1{\cdot}2 \times 10^{-14}$, or slightly over one ten-millionth normal. It might be supposed that so small an ionisation might be neglected, but in the case of salts of acids or bases of which the ionisation constants are so low as to approach this figure the results are very important. Carbonic acid, for instance, is such an acid, and many of the amino-acids present in proteins come into the same category, though their salts with strong bases ionise freely. Sodium carbonate thus ionises into Na^+ and CO_3''. When the CO_3'' comes in contact with the H^+ ion of the water it at once combines with it to form almost unionised H_2CO_3, and so goes out of the equilibrium, and further water is ionised to restore its H^+ concentration to the old amount, and this process is repeated till the acid reaches such a concentration that its ionisation is equal to that of the water. During this process the OH and Na ions accumulate in electric equilibrium, and as alkalinity is due to the OH ions, the solution becomes strongly alkaline. A similar result occurs with a little ionised base such as alumina and a strong acid; the H ions accumulate, and the solution becomes strongly acid, as in the case of aluminium sulphate, although in both cases the salts are chemically normal.

The salts of "strong" acids with "strong" bases are not perceptibly hydrolysed, and so whether methyl orange or phenolphthalein be used as indicator, the change of colour is practically simultaneous, and so soon as sufficient acid is added to neutralise the base the solution becomes instantly alkaline, but with "weak" acids or bases the change of colour is very gradual, and there is a wide interval between the two indicators, which in former times was supposed to show that the combination was not "chemical," and that there was no definite point of saturation; or such ideas as that of a series of valencies successively neutralised was adopted to account for it. The simple reason is that owing to salt-hydrolysis[1] the increase of H^+ or OH' concentration is

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[1] The amount of hydrolysis may be deduced from the mass-law and the ionisation-constants of the substances concerned, but except for monovalent acids and bases, only one of which is weak, it becomes very complicated, and the reader is referred to the larger books on physical chemistry. Where both acid and base are weak the amount of hydrolysis is not affected by dilution, but in the simpler case of only one weak monovalent acid or base it follows the same dilution law as ionisation (p. 99), which may be expressed by the equation $k' = \left(\frac{m^2}{1-m}\right)v$, where v is the volume, m the proportion of hydrolysis to the whole, which is taken as 1, and k' a hydrolysis-constant, different from the ionisation-constant k, but bearing the relation to it that $k' = \frac{k}{k_w}$, where k is the ionisation-constant of the weak acid or base, and k_w that of water, $1 \cdot 2 \times 10^{-14}$. Thus, if the hydrolysis-constant is known, the ionisation-constant can be calculated from it, and *vice versa.* (*Cp.* p. 98.) For many purposes the simple formula, $m = \frac{k}{x+k}$, or $1 - m = \frac{x}{x+k}$, where m is the proportion hydrolysed (the whole being taken as unity), x the hydrion- or other ionic-concentration, and k either the ionisation- or the hydrolysis-constant as may be required, is more convenient, and is merely another form of the same equation. (*Cp.* App. B.) The curve rises rapidly at first, and gradually becomes horizontal, only reaching the value of unity at infinite concentration, but if the hydrolysis-constant is known, unity can be calculated, or very approximately estimated, by plotting on curve paper. If the constant is correct, unity is the equivalent combining weight of the substance.

a very gradual one, and as each indicator changes colour more or less gradually over a certain range of H^+ concentration, there is often no definite end-point. Phenolphthalein changes slightly on the alkaline side of true neutrality, methyl orange on the acid side, and thus there is a considerable range of hydrion concentration between the two. Phenolphthalein is therefore suitable for the titration of weak acids, since it does not react till their neutral point is actually passed, and methyl orange for a similar reason for weak bases.

The Determination of Hydrion-concentration.—It has been shown (p. 100) that mere titration furnishes no guide, or at most a rough one, to the "true acidity," which depends on the actual hydrion-concentration, and which is really the cause and measure of most of the changes which take place in tanning. There are at present only two methods which are available for this purpose; the electrometric, which, though very exact, requires complicated and expensive apparatus and considerable skill in its use, and the colorimetric, which, though less exact, is sufficiently so for most technical purposes, and is easy and inexpensive, and will therefore be first described. It has been mentioned in the last section that different dyestuffs used as indicators change colour at different hydrion concentrations, and do so gradually over a certain small range, so that by suitable choice the whole range of the small concentrations where hydrion-determination is important can be covered. For this purpose an indicator is often most useful which does not change too suddenly but covers a considerable range of concentration, while for an ordinary indicator in titration the change cannot be too rapid. It is obvious that in a colourless liquid all that is necessary is to place the liquid to be measured, and another of known hydrion-concentration, in two similar tubes with equal quantities of the selected indicator, and vary the known concentration till the two exactly match. In practice it is found more convenient, and usually sufficiently accurate, to have a series of, say, ten liquids of graduated and known hydrion-concentration, and to compare these successively till a match is made, or a pair found between which the tested liquid can be placed. Where it is required, as will often be the case, to bring a liquor to a definite degree of true acidity, this can be done by gradually acidifying the liquor with some weak acid till it matches the standard tube, and adding the same proportion of acid to that in use on the large scale. Unfortunately tannery liquids are rarely colourless, which has proved a bar to the use of the method until the invention of the "Comparator" by Walpole,[1]

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[1] See Appendix D.

which overcomes the difficulty by a very simple means. Instead of two tubes, four are used in pairs one behind the other in front of a suitable light (often a Welsbach gas-burner). In the two front tubes the liquor to be tested, with its indicator, and the standard colour liquid are placed, while behind the latter is a tube of the unaltered liquor, and behind the liquor-tube with the indicator is a tube of pure water, so that the colour of the liquor is exactly balanced.

With regard to the electrometric method, only the principle can be explained here, and for working details the reader is referred to other books.[1]

If we imagine two galvanic cells, both alike, say consisting of copper in saturated copper sulphate, and zinc in zinc sulphate solutions of equal concentration, with their positive poles opposed to each other, and their negative also connected, there will be obviously no current produced, but if the zinc sulphate solutions are of unequal concentration, a current will be set up in such a sense than zinc will be dissolved in the weaker solution till its osmotic pressure and concentration becomes equal to the other, that is, a positive current will pass from the anode of the weaker to that of the stronger cell until equilibrium is restored. It is obvious that the energy which produces this current is the difference of ionic osmotic pressures, and as the relation between these two forms of energy is known, the electric pressure or "potential" can be calculated from the ionic concentration, or *vice versa*.

In our particular case it is the ionic concentration of the H^+ ion which we have to determine, and clearly if we could use a plate of metallic H in place of the Zn, we could accomplish it by a similar arrangement. This cannot of course literally be done, but it is found that if we bubble hydrogen gas over a plate of platinum coated with platinum black, enough gas is absorbed

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[1] *Books of reference as to electrometric methods.* Ostwald-Luther for practical details of measurement. *J.S.C.I.*, 30, 1911, p. 3, Wood, Sand, and Law describe the use of a very convenient but somewhat expensive apparatus designed by Dr Sand for the determination of H^+ concentration in puers and tan liquors. The same apparatus is figured and described in Wood's book on *Puering, Bating, and Drenching of Skins* (Spons, 1912). The simple bridge-wire method described in Ostwald-Luther is at least equally accurate, but not being self-contained, is not quite so convenient to handle. Before the war good and cheap apparatus could be got of Köhler, Leipzig. Sand's apparatus is made by Griffins. An excellent discussion of the subject, and many valuable hints on practical work, and also on the use of indicators, may be found in Sörensen's *Comptes-rendus du Laboratoire de Carlsberg*, 8, 1909 (Hagerup, Copenhagen).

to make it behave like one. In place of the copper and copper sulphate we use mercury and a solution of potassium chloride mixed with powdered HgCl (calomel), which is very difficultly soluble, and keeps the solution saturated, as it is found that this arrangement gives a still more constant electromotive force than the copper. If we imagine a pair of such galvanic elements opposed to each other, each composed of a similar mercury electrode and a hydrogenised platinum plate immersed in an acidified solution, we can see that these two solutions must be of exactly equal acidity (hydrogen-ion-concentration) if no current is to be produced. If instead of adjusting the solutions we measure the potential (or electric pressure) between the two cells which tends to produce a current, employing a known hydrion solution in one cell, we can calculate the concentration in the other.

A still simpler way is to measure the potential produced by a single element consisting of a calomel electrode and a hydrogenised platinum plate in the acid solution, having previously determined the potential produced with a normal acid solution, and this is the method now generally used. Sörensen has found that the potential of such an element with decinormal potassium chloride solution and calomel in the negative, and acid, normal with regard to the ionised hydrogen in the positive cell (corresponding to $P_H = O$ on the Sörensen scale), is 0·3377 volt, and as the potential rises with the dilution of the hydrion solution, the potential for any given dilution is $\text{Pot.} = 0{\cdot}3377 + 0{\cdot}0577 \times P_H$, or conversely, $P_H = \frac{\text{Pot.} - 0{\cdot}3377}{0{\cdot}0577}$ at 18° C.

The Logarithmic Expression of Numbers.—For the expression of ordinary numbers, such as we use in everyday life, the ordinary Arabic notation is sufficiently convenient, but when we come to deal with very large or very small numbers, as is frequently necessary in science, it becomes very cumbrous. It is much shorter to write £4×10^9 than £4,000,000,000, and it means quite the same thing, and if we are to accumulate debt at our present rate we may have to adopt it! The explanation of the expression is quite simple—10 multiplied once by itself (its 2nd power) is 100; 10 multiplied six times by itself is a million, and so on, and the exponent 9 used in the illustration means that nine 0's have to be affixed to 1 to express it in the ordinary way. What is rather more puzzling to the non-mathematical is the expression 10^{-9}, but it is really equally simple. A minus exponent is a reciprocal; thus 10^{-9} is $\frac{1}{1000000000}$ or 0·000000001, that is, the 1 (or the first significant figure whatever it may be) is in the 9th place of decimals.

In Sörensen's exponential or logarithmic notation, $P_H = 3$ means that the divisor of a solution normal as regards hydrogen-ions, or containing 1 eq. = 1 grm. of ionised hydrogen per liter, is 10^3 or 1000, or that the solution is N/1000, and so on. As, however, it is inconvenient to have to prefix a multiplier, say $1 \cdot 5 \times 10^3$, to signify a N/1500 solution, the fractional power of 10, which equals 1·5, or, in other words, the Briggsian or common logarithm, is used, and we write $P_H = 3 \cdot 18$, 0·18 being the log. of 1·5. Thus the exponent of the 10 is simply the index of the log., and the decimals are the mantissa.

The following short table giving the number from 1 to 10 and the mantissæ of the corresponding logarithms will be sufficient for the conversion of the Sörensen exponential scale into the divisors of normality:—

Number	1	2	3	4	5	6	7	8	9	10
Logarithm	0·00	0·30	0·48	0·60	0·70	0·78	0·85	0·90	0·95	1·00

Hydrion-concentrations.—The concentrations of both hydrions and hydroxyl-ions in pure water is about $1 \cdot 1 \times 10^{-7}$ at 18°, and on the exponential scale P_H and P_{OH} each equal 7·07, and this is the point of true neutrality, and solutions of a greater P_H are alkaline. The ionisation-constant of water k_w is the *product* of these, and about $1 \cdot 2 \times 10^{-14}$, or on the exponential scale 14·14, since the addition of exponents or logarithms is equivalent to the multiplication of their numbers; and this product is constant in water and all dilute solutions. Consequently if we raise the concentration of hydrions to normality by the addition of acid, that of hydroxyl-ions will fall to zero, and *vice versa* if we add alkali. Since the determination of hydrions is much easier and more exact than that of hydroxyl-ions, it is customary to express both acidity and alkalinity as hydrion-concentration, but the value of P_{OH} can always be found by subtracting P_H from 14·14 (or for ordinary purposes from 14). The convenience of the exponential scale is obvious in practice, since, when we come to very great dilutions, it is rare that we can attain to much greater accuracy than to say whether we are dealing with millionth or 10 millionth dilution.

CHAPTER X

COLLOID SOLUTIONS AND THE COLLOID STATE

The Colloid State.—The term "Colloid" (signifying "gluey") was first applied by Graham to the class of bodies of which glue and gum are typical examples, and of which the solutions have no definite point of saturation, and have little, if any, tendency to diffusion or osmotic pressure. It has since been extended to include what were earlier called "pseudo-solutions," in which the dissolved substance is contained, not as molecules, but as extremely small particles permanently suspended in a liquid. It has been more recently shown by von Weimarn, Hopkins, and others that many typical colloids, such as egg-albumin and gelatin, can be crystallised, while such definitely crystalline substances as even common salt can be obtained in the colloidal form by precipitation in liquids in which they are sufficiently insoluble, so that it is now more proper to speak of the "colloid state" than of colloids as a separate class.

The pseudo-solutions, now more frequently called "suspension-colloids," or simply "sols," concern us principally because basic chrome, iron, and alumina solutions and basic salts generally are possibly sols of the respective oxides in the solution of normal salt, though this point requires further investigation. Sols may be obtained in a variety of ways: by precipitation in liquids in which the precipitate is extremely insoluble, by "peptisation" or the bringing of precipitates already formed into the sol condition, or by the electric spraying or electrolysis of metals, but the essential point seems to be their insolubility in the liquid medium, as otherwise the smaller particles would dissolve and recrystallise on the larger ones, and the solution would be precipitated. Very typical are the colloid solutions of metallic gold obtained by the reduction of very dilute solutions of gold chloride by substances which do not at the same time form electrolytes in the liquid. These sols are red or deep purple, and perfectly transparent, and pass through filter-paper like true solutions, but they can be shown by the "ultra-microscope" of Zsigmondy to be coloured by actual particles of metallic gold, of extreme smallness, and in rapid vibratory (Brownian) motion, caused by the collisions of the molecules of the solvent in their heat-vibrations.[1]

The suspended particles, though in constant motion, are prevented from actual contact by electric charges, which, being of the same sign, cause them to repel each other and prevent their coalescence, but the addition of an electrolyte such as common salt to the solution causes their discharge, and the sol coagulates and precipitates. This is probably due to the electric adsorption of the ion of opposite charge to that of the particle, and as a rule the higher the valency of this ion the greater the precipitating effect. Additions of very small quantities of certain colloids, mostly proteins, greatly lessen, or even prevent, this precipitation, and are hence called "protective colloids." Of these gelatin is perhaps the most powerful, 1 mgr. protecting a liter of gold-sol from the precipitating effect of a large quantity of salt, probably by coating the particles. The precipitates from sols are often called "gels," but the term must not in any way be confounded with *jellies*, which have quite different properties. The addition of small quantities of protective colloids greatly favours the formation of colloid sols, and the presence of gelatin has this effect in the preparation of photographic emulsions.

While electrolytes in quantity rapidly precipitate sols, the presence of traces seems essential to their formation, probably because ions are necessary to give the electric charge. A colloid solution of iron oxide in water is obtained by dialysing ferric chloride through a parchment-paper membrane, through which the iron oxide will not pass, while the hydrochloric acid produced by the hydrolysis readily does so, but however long the process is continued, a trace of Cl is always found in the colloid solution. This solution has been used as a tonic under the name of "Fer Bravais," and is quite clear, and of a dark brown colour, but

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[1] The ultra-microscope in its original, and still most perfect, form consisted of a glass-sided cell on the stage of the microscope, the liquid in which was brilliantly illuminated by a thin, flat horizontal beam, concentrated on it by a powerful and accurately adjusted condenser. As the thickness of the beam was exactly known, it was possible to count the particles in a known volume of liquid. A much simpler, but less quantitative method is to concentrate the light in the liquid under a cover-glass on an ordinary slide by a substage condenser of very wide angle, so that the brilliantly illuminated particles are seen on a perfectly dark ground, since the centre of the condenser is darkened, and the light is projected from all sides at such an angle that it cannot pass through the cover-glass on account of total reflection. Probably the best of these is the Zeiss "cardioid condenser," but for many purposes a good "paraboloid" answers well, and is somewhat easier to manipulate. The illumination of ordinary dark-ground condensers is insufficient.

is extremely unstable, being precipitated immediately on heating, or even on dilution. It is highly probable that colloid solutions of alumina and chrome oxide might be produced by similar means, and the subject will be again alluded to in dealing with chrome and with the theory of tannage.

Mutual Precipitation of oppositely charged Colloids.—It has been stated that the colloid particles have electric charges, probably from attached ions, and that the repulsion of these similar charges prevents their contact. If, however, a colloid sol of + charge be mixed with one of — charge, the particles attract each other and produce mutual precipitation, and if the quantities are electrically equivalent, the precipitation may be quite complete, but if one or other is in excess, neither is usually completely separated. It is probable that the precipitation of gelatin by tannin is an instance, and in this case, if the gelatin be in excess, a portion of the tannin remains dissolved. Many dyestuffs are colloidal, and we know that basic dyes are constantly precipitated by acid ones. It is hard to make any distinction between such reactions and those which are strictly chemical, since both are due to the combination of + and — ions, but the colloidal charges vary with the size of the particles, and thus are less definite than those of single ions.

Kataphoresis and Electric Osmose.—If an electric current be passed through a colloid sol, the — charged particles will move towards the + pole or anode, and the + charged towards the — pole or kathode, that is to say, towards a region of higher electric charge of the sign opposite to their own. Arrived at the pole they usually become discharged, and often form a clot of precipitate, but cases are known where they take fresh charges of the opposite sign and return towards the other pole, sometimes meeting and precipitating oppositely charged particles midway. The particles thus behave precisely like the ions in electrolysis, and of course like them possess an electrolytic conductivity, though a small one. Electric osmose is the converse of kataphoresis. If a cell is divided into two compartments by a porous partition with an electrically charged surface (as, for instance, earthenware, powdered glass, bladder, or parchment paper) and a current be passed through, the liquid will flow through the partition in the opposite direction to that in which the material of the partition would have moved if it were in the form of suspended particles, and if it cannot escape, will rise considerably above the level of the side from which it flows. This effect explains the theory of electric tanning so far as it has one. If an alternating current is used there will be no steady flow, but merely a vibration;

and if a continuous, the process is complicated by electrolytic decomposition, and indirect destruction of tannin.

Kataphoresis is important as being the simplest mode of determining the sign of the charge on suspended particles. The experiment is usually made in a U-tube. If the particles are not visible to the eye, their concentration in the two limbs of the tube is determined by analysis. The following table gives the sign of the charge on a few of the commoner colloids. The charge is often reversed in acid and alkaline solutions, and with amphoteric bodies changes at the isoelectric point (see p. 111).

Positive Solutions (to kathode).	Negative Solutions (to anode).
Hydroxides (of Fe, Cr, Al, Cu, etc.).	Metals (Au, Ag, Pt, Pd, Ir, Cd).
Some metals, Pb, Bi, Fe (probably hydroxides in water).	Metallic sulphides. Silver halides.
	Proteins in alkaline solution.
Proteins in acid solution.	Silicic acid in alkaline solution.
Silicic acid in acid solution.	Starch, mastic, caramel, resin, shellac.
	Iodine, sulphur, selenium, tellurium.
	Oil emulsions.

Natural Organic Colloids.—These, proteins, gums and the like, are now frequently styled "emulsion-colloids," on the assumption, by no means proved, that their apparent solutions are fine emulsions of one liquid in another. They have many analogies with the suspension-colloids, but also marked differences, and it is not unlikely that their colloid character arises from quite different causes. They all have large molecular weights, and mostly a tendency to polymerisation (the grouping of several or many molecules together), and their solutions have large viscosity, and not unfrequently take the form of consistent jellies (not gels). Their solutions are not precipitated by small quantities of electrolytes, and the "salting out" which occurs when some salts are added in large quantities is probably quite a different phenomenon. Their solutions generally show at least traces of reflected light (Tyndall effect) when a powerful beam is passed through them, but it is only rarely that separate particles can be detected by the ultra-microscope, and these are possibly accidental impurities. Many of them, especially the proteids, are amphoteric, or capable of acting both as acids and bases, as will be readily understood from their chemical constitution (see Chapter XI.). Their molecules or particles possess electric charges, but there is a point, corresponding to a definite alkalinity or acidity (p. 118), at which they are neutral, and on the acid side of which they behave as bases and on the alkaline as acids, but never both at once. This is called the "isoelectric point," and is not usually exactly at the neutral point of water. Generally this point is also that of minimum swelling.

Viscosity is so important a characteristic of these solutions that it demands special consideration. The viscosity of oils, glycerine, and more or less of all liquids, is simply internal liquid friction impeding their rate of flow, and is usually, and properly, measured by the time required for a measured volume to pass through a capillary tube under a definite pressure. This is the construction of all ordinary viscosimeters, and is quite satisfactory even for gelatin solutions above the melting point of their jellies, but as this is approached and passed, even very dilute solutions, apparently quite liquid, suffer a rapid increase in viscosity, which is apparently of a different character, and arises from jelly-structure. Such a solution, if passed through a capillary viscosimeter a second time, always shows a lower viscosity than at first, and the viscosity is also much lowered by shaking or violent agitation, pointing to the breaking up of some structure (*cp.* also p. 113). A noteworthy fact about viscosity of the proteids is, that with increase of acidity it usually rises to a maximum and then again falls, and that the maximum appears to be at approximately the same P_H as that of maximum swelling, where this has been determined by other methods, while it is at a minimum at the isoelectric point.[1]

Dialysis and Ultra-filtration.—Colloids will not, as a rule, pass through colloidal membranes, such as parchment paper, bladder- or gold-beaters'-skin, or through thin films of gelatin jelly, or filter-paper soaked in gelatine solutions, while crystalloids generally pass freely. This affords a means of separating colloids from crystalloid impurities. The colloid solution is, for instance, placed in a parchment-paper drum and floated on water, which is frequently renewed. Jellies form their own dialyser. Swollen gelatin which has been treated with a weak acid to bring calcium sulphites and phosphates into solution can be freed from them by washing on a canvas-bottomed tray floated in water.

Bechhold's[2] method of ultra-filtration is filtration under slight pressure through filter-paper which has been impregnated with a porous film of collodion or gelatin. The degree of porosity can be regulated by varying the strength of the collodion or gelatin

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[1] Loeb, *Journ. Gen. Physiol.*, 1918–19, vol. i., pp. 39, 237, 363.

[2] *Zeit. Phys. Chem.*, 60 (1907), p. 257, and 64 (1908), p. 328.

solution, so as to allow some colloid particles to pass while retaining others. For details the original paper must be consulted.

Fractional precipitation is another means which can sometimes be employed with success for the separation and purification of colloid solutions. Sulphates of ammonia or soda are frequently employed for this purpose. If added in sufficient quantity the whole of the really colloidal constituents may be flocculated and separated, generally carrying down with them some non-colloidal matter, which may be removed by re-solution and re-precipitation. If the quantity of the precipitant added be insufficient to precipitate the whole of the colloids, the first precipitate will be mainly of those most easily dehydrated, while those with a greater attraction for water can be brought down by a further addition of the salt. Of course neither of these fractions is a pure individual proteid, but this may be approached by repeating the operation, perhaps with a less or different addition of the salt. The precipitation seems to be one of simple dehydration, and the salt retained in the precipitate may be removed by dialysis. The theory of this " salting out " is somewhat uncertain. It is possible that it is due to the hydration of ions withdrawing the water from its function as a solvent, or that the jellies, though permeable to the ions, are not so to the unionised salts, the osmotic pressure of which therefore expresses the water from them, just as in the case of dehydration by alcohol, which does not ionise to any extent. Proteins are usually insoluble in water at the isoelectric point.

Jellies.—Many organic colloids remain in more or less viscous solution even at low temperatures, but others, including gelatin, set to a more or less coherent jelly on cooling. Much discussion has taken place as to the physical structure of these jellies, the earlier school of colloid chemists holding with Bütschli and van Bemmelen that they had a sponge-like structure with open pores which might even be made visible under the microscope, while the adherents of the emulsion-theory of organic colloids have held that they consisted of globules containing water (or some other solvent) separated by a liquid consisting of a weaker colloid solution. It has, however, become evident, especially since the work of the writer on the gelatin equilibrium with acids, that neither of these theories can be maintained, at least in their original form, and that the net-like structure, if it exists, cannot be of more than molecular dimensions, since the whole mass is in chemical equilibrium with the surrounding solution, and must therefore be within the sphere of molecular attractions. The prevailing idea at present seems to be that of a network of molecules, possibly crystalline. From Chapter XI. it will be seen that these molecules are probably long chains of amino-acids, which would lend themselves to such a structure. Jellies also present striking analogies in their behaviour with external solution to that of two immiscible solvents with a third substance soluble in both, and probably the safest position is to regard them as solid, or semi-solid solutions without theorising too much at present as to their ultimate structure.[1]

In the following pages attention will be particularly directed to the gelatine jelly, not only because it specially interests us by its close relation to skin, but because it is typical of most other gelatinising colloids. A solution of gelatine heated above 70° C. undergoes chemical changes which gradually diminish its setting power, which after continued boiling entirely disappears, but below 70° the change from solid to liquid seems quite reversible. A solution of good gelatine at 70° shows few or no ultra-microscopic particles, and only a very slight Tyndall effect, and may well be an actual solution of large molecules. As it cools, both the Tyndall effect and the viscosity increase, but only slowly, owing to the sluggish motion of the particles, and it is often some days before the full effect of a given temperature is reached. As the temperature nears the setting point the rise of viscosity is much greater, though even after complete setting the firmness of the jelly continues to increase for many hours or even days. The viscosity near and below the setting temperature seems to be of a different type to the ordinary frictional viscosity of higher temperatures, and is apparently due to some sort of structure, as it is diminished by vigorous stirring, or even by passing through an ordinary capillary viscosimeter.[2] Solutions so dilute as to be apparently quite liquid below the setting point still show these effects, and a disc suspended in the liquid by a torsion wire will only move a short distance and take up a permanent position at a slight torsion. Such liquids also show the dipolarising effects of strain in the polariscope if examined in the annular space between a fixed and an interior rotating cylinder

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[1] Certain organic substances which ultimately form masses of needle-like crystals take at first a jelly-like condition, and even masses of crystalline salts have often a considerable resemblance to jellies. Gelatin can be crystallised by very slow evaporation, and some observers have noted resemblance to thread-like crystals in the ultra-microscope. Soaps form very decided jellies, but are alkaline salts of fatty acids, and decidedly crystalline.

[2] *Cp.* Arisz, *Kolloidchem. Beihefte*, 7, 1, 1915, long abstract in *J.S.L.T.C.* Arisz describes some curious results in heating and cooling solid jellies, but as these contained glycerine, it is difficult to draw conclusions.

(Kundt, *Wied. Ann.*, 1881, 13, p. 110), which is quite absent in much more viscous liquids such as glycerine and sugar syrup, though it is shown by fatty oils.

If we place a sheet of dry gelatine in water it swells, absorbing perhaps seven or eight times its weight of water, but does not appreciably dissolve. A condition of equilibrium is reached when the osmotic pressure within the jelly is equal to the sum of the cohesive attraction of the gelatine for itself and the osmotic pressure of the water outside. An increase of the cohesion of the gelatine would tend to make it contract and expel part of the water, and this contraction would tend further to increase the cohesion of the gelatine. The equilibrium is therefore a very unstable one, and slight causes might be expected to produce great changes in the degree of swelling, which is indeed the case. If we increase the temperature we diminish the cohesion of the gelatine, till at a point it becomes less than its attraction for the water, and the jelly suddenly loses its solid condition and dissolves. The melting point of good gelatine varies somewhat, but is usually between 25° and 30° C. With glues and inferior gelatines it is often much lower owing to the presence of gelatoses, and forms a useful test of commercial quality.

The absorption of water by dry colloids (including gelatine) is accompanied by contraction of volume (compression of the water absorbed or of the colloid itself) and by evolution of heat, and, as has been pointed out by Körner,[1] it is opposed by increase of temperature, but at the same time the cohesion of the jelly is decreased, which favours swelling. Solution, on the other hand, absorbs heat, and is therefore favoured by rise of temperature. The problem is therefore very complex, and the actual result probably varies with the degree of hydration of the jelly.

If we place the swollen jelly in alcohol, it parts with water and contracts. The gelatine and alcohol are not mutually soluble; the sum of the attraction of water for alcohol and the cohesive attraction of the gelatine is greater than the attraction of the latter for water, and as the alcohol cannot pass into the gelatine, the water passes out, and the jelly contracts. The greater the concentration of the alcohol, the more completely is the jelly dehydrated, and in strong alcohol it may become quite hard and solid. This method of dehydration was adapted by Stiasny for estimating the water content of pelt. If we like to express the same facts in language more familiar to the modern chemist, but perhaps less clear to the non-chemical reader, we may say that the alcohol exerts an osmotic pressure outside the

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[1] *Beiträge zur wissenschaftlichen Grundlage der Gerberei*, Freiberg, 1899.

gelatine, but little or none inside it, and therefore the water is squeezed out, till the osmotic pressure is equal in both the jelly and the alcohol. The jelly is a true "solid solution" of water in gelatine; we may regard either of the two constituents as the solvent. Exact parallels may be found in the distribution of a third substance between two immiscible solvents (see p. 93), say, alcohol between water and benzene.

The osmotic pressure of alcohol may be demonstrated in a very simple way, taking advantage of the fact that a film of jelly is permeable for water but not for alcohol. If the experiment described on p. 96 be made by placing alcohol in a cell previously washed out with a gelatine solution, and the cell be placed in water, the water will pass into the cell, and the alcoholic solution will rise many feet in the vertical tube. The insolubility of gelatine in alcohol may be made use of for its estimation. If at least three times its volume of absolute alcohol be added to a solution containing gelatine, the latter will separate as a solid mass on a stirring rod, or on the sides of the beaker, and may be washed with further portions of alcohol. The method is useful in the proximate analysis of gelatine lozenges and "jelly squares," roller compositions, hectograph masses, and the like, and for the determination of true unaltered gelatin in glues and commercial gelatines (see p. 150), but it must be remembered that many other colloids are also precipitated by alcohol.

If hide be treated with alcohol, as in Knapp's experiment (p. 575), the action is precisely the same as has been described with gelatine-jelly. The water is withdrawn, first from the spaces between the fibres, and then from the fibres themselves, and the skin dries with the fibres isolated and non-adherent, and is in fact converted into a sort of leather, which, however, returns to raw pelt on soaking in water.

The action of solutions of sugars, glycerine, and the like is in principle similar to that of alcohol, but more complex, since in general these bodies are soluble not only in the water, but in the gelatine or hide-fibre, so that their effect cannot be foretold, though usually it tends towards contraction rather than swelling. In general terms the equilibrium is a balance of the attraction of the water and the sugar for the gelatine, against the sum of their mutual attraction in the solution outside and the resisting cohesive force of the gelatine; and will depend not only on the nature of the substances, but on temperature and concentration.

The action of acids, alkalies, and salts on gelatinous fibre is yet more complex, since not only electrolytic dissociation, but actual chemical combination comes into the question. The detailed chemical constitution of gelatine is as yet uncertain, but it is known (see Chapter XI.) to consist of chains of amino-acids, linked by the carboxyl of one to an amino-group of the next, leaving an amino-group NH_2 at one end of the chain and a carboxyl (COOH) at the other. Hence hide-fibre absorbs both acids and bases with great avidity, so much so that the sulphuric acid of a decinormal solution may be completely removed by hide, leaving only water without a trace of acid recognisable by litmus. Alkalies are absorbed in a similar way, and in both cases the gelatine or gelatinous fibre acquires a greatly increased power of absorbing water, and consequently of swelling. Familiar cases of this are the swelling of hide by acid and by lime, and in neither case can the added substance be removed in any reasonable time by mere washing with water. Hence to free hides from lime or acids it is necessary to neutralise the alkali with acids (see p. 203) or the acid with chalk or alkalies (p. 206).

If hide or skin, previously swollen with acid, be placed in a strong solution of common salt, it is dehydrated and the swelling completely reduced, and, as in Knapp's experiment with alcohol, it is converted into a sort of white leather, which however swells again strongly if placed in water. This is the cause of "pickling," which is described in Chapter XV. A similar action takes place with acid gelatine, which becomes quite hard and horny.

When dry gelatine is placed in water, it absorbs it with great avidity at first, but afterwards more slowly, forming a jelly. Dry hide behaves in the same way (though the jelly is one of collagen, and not strictly of gelatine), so that the fibres of wet hide are threads of colloid jelly. Water is also absorbed by the hide *between* the fibres by capillarity.

It may be taken as fully proved that gelatine acts as a base with dilute acids, forming a colloid salt which ionises into a colloid kation and the anion of the acid, and which hydrolyses with excess of water back to gelatine and the original acid, so that the base can only be fully saturated in presence of excess of acid, and an equilibrium is formed dependent on the H^+ concentration of the acid, which determines the proportion of uncombined gelatine and of free acid to that of saturated gelatine salt. As the latter rises gradually with the concentration of the acid, there is no point of neutrality to indicators, a fact which led earlier chemists to deny the existence of a definite compound.[1]

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[1] T. Brailsford Robertson in his book on the *Physical Chemistry of Colloids* (Longmans, London and New York, 1918) admits the salt-forming character of proteins, but believes that it is not the terminal amino and

The point of saturation can, however, be determined by calculating the infinity-value of a plotted curve.

If we place gelatine in dilute acid (say N/100 HCl) it swells much more than in pure water, under favourable circumstances to fifty times its original weight, though as the acid concentration is increased beyond a certain *optimum* point, the swelling steadily diminishes in a sort of hyperbolic curve, the greatest swelling being obtained with acid of H^+ concentration about $P_H = 2{\cdot}4$. With pure water it only swells to seven or eight times its original weight.

It must be understood that every mass of gelatine jelly or every gelatinous hide-fibre in an acid solution of any definite strength is in equilibrium with the surrounding solution, that is, that it contains water, gelatin-salt, free gelatin, and free acid in such proportions that there is no tendency for either acid or water from the surrounding solutions to pass into or out of the jelly, though both can pass freely through its surface.

In applying these facts to the problem of swelling we may simplify the task by neglecting the un-ionised substances, which in this case passing freely in or out of the jelly, affect it only indirectly, and by confining our attention to the ions themselves which are proved to be the real active agents.

Admitting the existence of gelatin salts, we have to consider the effect of their ionisation on the swelling. The gelatin-ion remains colloid, that is, it tends to agglomerate into masses or large particles which do not diffuse, and consequently exert no appreciable osmotic pressure, so that the ionised salt still remains a jelly or a colloidal solution. The anion, in this case the Cl ion, on the other hand, tends to diffuse and exerts osmotic pressure, but cannot leave the jelly on account of the electro-chemical attraction of the gel-ion. It therefore swells the jelly, thus drawing into it the outside acid solution. This, however, contains the hydrogen and chlorine ions of the ionised acid in equal quantity, and while the former can enter the jelly without hindrance, the latter are opposed by the osmotic pressure of the ionised Cl′ already inside. The results are that the acid which enters is less

carboxyl groups which enter into combination, but the NH and CO groups at the linkage of the different amino-acids which form the protein, and that consequently the colloid salts ionise into two colloid ions, and do not hydrolyse. It is possible that this may be true of some other proteins, or even of salts of gelatin with more concentrated acids, though it is not universally admitted, but it is certainly not the case with the monacid salts of gelatin with which we are concerned, as the chloride, for instance, certainly does ionise Cl ions, and does hydrolyse. This is also confirmed by the work of J. Loeb.

concentrated than that outside, that the total concentration of Cl′ is greater, and that of H^+ less in the jelly than in the outer solution, and as the acid H cannot enter without its associated Cl, a layer of positive H^+ forms outside the jelly surface, opposed and balanced by a similar layer of negative Cl′ within. Thus the two sides of the surface are in different electrical condition, or, in electrical language, there is a potential between them (Donnan's "Membrane Potential"),[1] and the surface-layer outside the jelly has a small + electric charge. If, instead of being acid, the jelly and outer solution were alkaline, say with soda, the gelatin, being amphoteric, would form a sodium gelatinate in place of a gelatin chloride, and the charge would be negative instead of positive. It is obvious that between these conditions there must be an "isoelectric" point of neutrality at which there is no potential charge. This does not necessarily occur at the exact acid and alkaline neutrality of water, but is dependent on the relative acid and alkaline affinities of the individual proteid. In gelatin and hide-fibre it is slightly on the acid side of neutrality $P_H = 4{\cdot}7$, or N/50,000 of actual hydrion-concentration, and this is the point of minimum swelling and greatest flaccidity of the skin, and the gelatin is insoluble and neutral, and on the acid side of the isoelectric point acts only as a base, and on the alkaline only as an acid. With regard to the actual tanning process, these charges are also of the highest importance, as negatively charged tannins can only combine with positively charged hide.

The osmotic pressure tending to swell the jelly is therefore a balance of two opposing forces, that of H^+ pressing in, and of Cl′ (or some other acid-ion) pressing out. Donnan has shown that when the jelly and its outer solution are in electrical and chemical equilibrium, the proportions of the two are connected by the law that the product H^+ multiplied by the Cl′ within the jelly must equal that of the $H^+ \times Cl'$ of the outer acid. Now the H and Cl of the outer acid are equal, while in the jelly Cl is in excess, and the *sum* of equals is always less than that of unequals which give the same *product*. Thus the *sum* of $4+4$ is 8, that of $8+2$ is 10, yet both give the *product* 16. Since the osmotic pressure is proportional to the *sum* of the ions, there is thus always a slight osmotic force tending to swell the jelly, greater as the two factors are more different. The greatest difference occurs when the quantity of free acid is very small and the chlorine in the jelly is almost entirely due to the ionisation of the gelatine salt, and it

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[1] Donnan and Harris, *J.C.S.*, 99, 1911, 1554. Donnan, *Zeits. f. Electrochem.*, 17, 1911, 572. Abst. *J.C.S.*, 100, 1911, 848.

is there that we get the greatest swelling. As the concentration of the acid and its quantity in the jelly increases, the difference becomes less and the swelling diminishes, and if we add salt also in large excess, the chlorine-ion on both sides is enormously increased, and the difference will, as in pickling, almost entirely disappear.

We have therefore accounted for the swelling force, and shown that as it increases or diminishes, the swelling does the same, and not merely in a general way, but mathematically and quantitatively, and that this force only quite disappears when the concentrations become infinite and equal. As, however, the swelling does not go on to infinity and solution, there must be some opposing force which, when the swelling reaches a definite equilibrium, is equal and opposite to the swelling force. This is apparently the attraction of one gelatin particle for another, the elastic cohesion of the gelatin; and it seems to follow Hooke's law generally applicable to elastic strains, in that it is proportional to the volume-extension.[1] The exact nature of such strains has not yet been determined, but in the case of colloids it may have something to do with the stretching or distortion of a molecular network. That it is sufficient to account even for the intense contraction under the influence of salt is shown by its magnitude when water is withdrawn by ordinary evaporation—a drying film of gelatin will often actually tear away the surface of glass to which it adheres. In another respect it resembles other elastic forces, since it diminishes rapidly and the swelling increases with increased temperature, till at the melting point of the jelly it apparently disappears, and the swelling goes on to complete or colloid solution. As, however, even in solution, the gelatin particles retain their electric charges, it is probable that, at least at temperatures below 70° C., they still continue as separate particles suspended in a surrounding liquid.

The experimental work on which these results were based was of a very varied character, including determinations of hydrogen and chlorine ion concentrations by electrical methods with concentration cells, and conductivities, but that principally used is

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[1] It is interesting to note that this law would result if the increase of surface, and consequently of surface-energy, were proportionate to the increase of volume. It is not intended to suggest that the surface is actually increased, but merely that the elastic cohesion is due to the same forces of molecular attraction. Since the surface-energy bears a simple relation to the heat of volatilisation, the volume elasticity of any body obeying Hooke's law must do so also, and the idea suggests itself, that it should also be related to the heat of liquefaction of the jelly.

of so simple a character that it may be given in detail. To avoid complications caused by the liquid capillarily retained between the fibres of actual hide, thin sheets of the best French bone gelatine were mostly employed, but the same methods can be applied to skin itself with very approximate results, and as it is desirable that these should be extended, the writer would welcome any co-operative work of an accurate character. The earlier experiments were only intended as preliminary, and Coignet's gelatine was used without further purification, but in the later work it was carefully purified, so as to be almost ash-free, by slightly acidifying with SO_2 to remove calcium sulphite and phosphate, and then washing for some days on nets with many changes of distilled water. This gelatine, however, must have retained small quantities of alkali, since its P_H in aqueous solution was 5·5, instead of 4·6 which corresponds to isoelectric gelatin. It was not found, however, that this had much influence on the determinations, since any traces of salts were pretty thoroughly removed by the considerable volumes of dilute acid employed in the experiments. As gelatin cannot be dried at a high temperature without materially affecting its solubility, air-dry gelatin was preserved in a stoppered bottle, and moisture was determined by drying a portion at 100° C. *in vacuo*, and this together with the traces of ash were allowed for in the weighings. Portions of 1 grm. were weighed into wide-mouthed stoppered bottles, and 100 c.c. of acid of accurately determined concentration was added, and allowed to stand with occasional gentle shaking for forty-eight hours, which was found to be sufficient to obtain practical equilibrium. The contents of the bottle were then poured into a funnel fitted with a finely perforated porcelain plate, covered with a clock-glass, and allowed to drain for two hours into a graduated cylinder. The volume subtracted from 100 c.c. gave that absorbed by the gelatin, any traces of moisture which the air-dried gelatin contained being negligible against unavoidable losses by evaporation and liquid retained on the surfaces of vessels. The quantity was also determinable as a check by weighing the swollen jelly. The concentration of acid in the cylinder, with which the jelly was in equilibrium, was determined by titration with sodium hydrate and phenolphthalein, and that absorbed by the gelatin was calculated. We thus ascertain the total acid absorbed by the gelatin and the volume of the swelling produced. The absorbed acid is not, however, entirely combined chemically with the gelatin, but a considerable portion exists as free acid imbibed in the swelling, and the proportion of this to the acid actually combined was still to be determined. To accomplish this, advantage was taken of the fact that the addition of neutral salt, while it reduces the swelling, and expels the merely absorbed acid, does not affect that actually combined with the gelatin. The swollen jelly was returned to the wide-mouthed bottle, and common salt was added so long as it would dissolve. After standing at least twenty-four hours with repeated shaking equilibrium was again established, and the jelly was reduced to a horny mass retaining only about 1·5 c.c. of the solution. The acid present in the expelled salt solution was again determined by titration, and calculated to the whole volume of the solution originally absorbed, remembering that 100 c.c. of a saturated salt solution only contain 88·6 c.c. of water. No appreciable error can arise from the assumption that the small remaining quantity of acid solution remaining in the jelly is of the same acid concentration as that expelled.[1]

We have thus the means of determining (1) the free acid unabsorbed which forms the "external solution" with which the jelly is in equilibrium; (2) the free acid absorbed by the jelly; and (3) the chlorine, ionised and non-ionised, combined with the jelly base. The sum of (2) and (3) can be further controlled by the titration of the dehydrated jelly with alkali hydroxide, which, with phenolphthalein as indicator, completely decomposes the gelatine salt. The table in App. B, p. 591, gives a series of such determinations with varying quantities of acid, and includes the whole of the results in the series of experiments to which they refer, which are more concordant than would be expected from the comparative roughness of the method.

In the dilute solutions used the ionisation of the gelatin chloride was found to be complete, or at least equal to that of the hydrochloric acid, which, to simplify calculations, was assumed to be wholly ionised, and we were thus enabled to give numerical values to the chlorion and hydrion concentrations, both of the jelly and of the external acid solution, and it was found that these, so obtained by calculation, agreed within experimental error with those obtained by the direct titration of the total hydrochloric acid in each (see p. 120).

It is obvious that from the results of these experiments two distinct series of curves can be calculated: those of relative con-

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[1] A saturated solution of salt at 15° C. contains 26·4 grm. of salt per 100 grm., or 31·9 grm. per 100 c.c., and has a sp. gr. of 1·204. As, owing to the presence of HCl, the solution cannot be fully saturated with salt, it is probably sufficiently accurate for the purposes of this calculation to assume that 100 c.c. contains 88·6 c.c. of the original solution, or 100 grm., 73·6 c.c.

centrations of the different constituents of the jelly and its equilibrium acid solution, which have been discussed, and a second series dealing with the actual quantities of each associated with 1 grm. or 1 mol. of gelatine, from which the composition of the gelatine salt and the combining equivalent of gelatine can be determined. When a strong acid combines with a strong base, the point of exact neutralisation is easily determined by titration with a suitable indicator; such as phenolphthalein; but where either the acid or the base is very weak, the salt hydrolyses again to free acid and base, and complete saturation of the one can only take place in presence of an excess of the other. Thus, in titrating gelatin with an acid, there is no point at which the indicator changes sharply, and the whole of the gelatin is only converted into chloride in presence of a large (and theoretically an infinite) excess of acid, a fact which led earlier chemists to suppose that no definite compound was formed. From the curves of concentration, however, we can determine the proportion of gelatin chloride formed as the acid is gradually increased in strength, and watch its rise, very rapid at first, but gradually becoming slower till it approaches a horizontal line at the point of complete saturation. To this point we cannot push it, since long before the acid has reached the requisite strength it begins to break up and dissolve the gelatin; but if we can find a mathematical expression which exactly reproduces the part of the curve which we can observe, we can calculate the point at which the horizontal would be reached. As the case is one of ordinary hydrolysis, it is probable that it will be covered by Ostwald's hydrolysis formula, which for the purpose in view is conveniently stated as $\frac{x}{x+k}$, where x is the concentration of the external acid, and k an ordinary hydrolysis constant. In addition to k, we have also the molecular weight as a second "unknown," by which the weight of 1000 mgr. actually taken for the experimental curve must be divided to bring it to molecular proportions. Both these might be found by simultaneous equations from different points in the curve, or by the approximation method described in the original paper (*Trans. Chem. Soc.*, 105, 1914, p. 319). The actual curve was very accurately reproduced by $y=\frac{x}{x+0{\cdot}0013}+\frac{x}{x+1{\cdot}05}\times\frac{1000}{839}$, which represents gelatine as a diacid base with a second very weak affinity, and a molecular, or at least equivalent, weight of 839. It seems probable, however, that gelatin is really monacid, and that the slight deviation of the curve was due to the splitting up of the gelatin by the more concentrated acid solutions; and Wilson, adopting this view, calculates an equivalent weight of 768, and an empirical formula which agrees extremely well with the results of ultimate analysis. Collagen or hide-fibre is supposed to differ from gelatin by the loss of the elements of water, and if so, its equivalent weight must be 750. It is not to be supposed that this is the actual weight of the molecule in a gelatin solution, which is probably often much larger, and probably variable by the union of several, or possibly many, equivalents (polymerisation). The equivalent represents the smallest proportion of gelatin which can combine with one equivalent of hydrochloric acid.

The methods which have been described have proved quite satisfactory with "strong" acids, and as regards hydrochloric acid have been pretty thoroughly carried out; but they fail to some extent with weak organic acids with which one can no longer assume complete ionisation of the salts, though that of the acids has been mostly determined. The addition of sodium acetate to gelatine acetate, for instance, fails to produce a dehydration nearly as complete as that of sodium chloride, so that the free acid in the jelly cannot be determined with much accuracy. The difficulty can be overcome with perhaps a slight loss of theoretical accuracy by the employment of sodium or potassium chloride as a dehydrating agent. This leads in the first instance to a quadruple equilibrium, in which the organic acid in the gelatin compound, from the large excess of the chloride, is practically entirely replaced by Cl, and the gelatin chloride thus formed is dehydrated as before by the excess of the Cl ion, the organic acid being titrated in the salt solution, and, if desired, the organic chloride estimated by gentle ignition with known excess of sodium carbonate, and titrating back. This complete replacement of a weak acid by a strong one is at first sight somewhat surprising, but is in strict accordance with the mass law, and explains the possibility of effective pickling by weak organic acids. It is necessary to add the salt to the original acid solution, as the use of an unacidified salt solution would cause extensive hydrolysis of the gelatin compound.

The action of neutral salts on the gelatinous tissue demands further study. Loeb[1] seems to think that on the acid side of the

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[1] *Journ. Gen. Physiology*, 1, 39, etc., 1918.

isoelectric point the gelatin combines direct with their anions, and on the alkaline side with their kations ; but to the writer it seems more probable that what takes place is merely a double decomposition, and substitution of an element of the salt for one already in combination with the gelatin, such as has just been described.

CHAPTER XI

THE CHEMISTRY OF HIDE

Chemical Constitution

Introductory.—Apart from small quantities of inorganic matter and of pigment, the chemical constituents of hide belong to that class of nitrogenous organic compounds called proteins or proteids, compounds of quite exceptional interest, since they form part, often the major part, of all living structures, and are involved in all life processes. Many proteins are familiar to everybody. The white of eggs, for instance, consists of water and protein, largely egg-albumin, a protein easily coagulated by heat as is evident whenever an egg is boiled. Milk contains a coagulable albumin, and casein, another protein. The former largely separates as a solid surface film when milk is heated, whilst casein is separated by the addition of small quantities of acid such as vinegar, or by a clotting ferment like that contained in rennet. All animal tissues are mainly protein. Skin, hair, nails and horns, muscle, etc., are composed of solid proteins, whilst blood contains, in addition to the suspended corpuscles and the fibrin, at least two other proteins in solution. In spite of the fact that chemists have been interested in proteins for over a century, we are still much in the dark in regard to their chemical constitution. A great deal has been accomplished, especially in the last twenty-five years, and we are now well acquainted with the simple chemical units of which proteins are composed. We know also the principal mode of linkage between these units. What we do not know is, first, the order or pattern in which the units are arranged—a matter of great consequence; and second, the number of simple units needed to form the protein unit or molecule. The chemical investigation of proteins has been found very difficult, since many methods widely applicable in other fields of chemistry have proved almost useless. When it is realised that proteins crystallise only in a few instances, and then with difficulty, that they have no definite melting points or solubilities, and that they are all very similar in chemical composition, it becomes obvious that ordinary methods of purification, etc., are quite inadequate, and that a new technique is required. On this account progress was for a long time very slow, but the interest of the subject has attracted many workers in recent years, with the result stated above.

Liebig's view was that one protein existed, and only one, and that the various substances which appeared to differ were simply more or less pure varieties of the one protein. It was by Liebig that a reliable method of ultimate organic analysis was elaborated, which when applied to proteins showed that a very great similarity in chemical composition existed amongst them. The amounts of carbon, nitrogen, and hydrogen do indeed fall within very narrow limits, as the following table of composition shows :—

Carbon . . .	51–55	per cent.
Hydrogen . . .	7	,,
Nitrogen . . .	15–19	,,
Sulphur . . .	0·4–2·5	,,

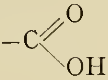
Proteins are known now whose composition falls outside the above figures, *e.g.* the protamines, but they are not commonly met with, and differ considerably in other respects from the general run of their class. It is, then, not surprising that Liebig thought of the proteins as one substance, difficult to obtain pure. Methods of arriving at chemical constitution were few in his day, and empirical composition was almost the only sure and definite knowledge obtainable. Mulder held a modified view. He regarded protein as one parent substance which combined in various ways with other things, *e.g.* sulphur and phosphorus, to give the different substances occurring in Nature. This view, like that of Liebig, though reasonable enough in its day, has had to be abandoned by reason of the cumulative evidence of subsequent work. Very many different proteins are now believed to exist.

The question may be asked, What are proteins? Although the chemical (ultimate) composition of most of them is characteristic of their class, yet that particular composition is not invariable, nor confined to proteins. The same empirical formula may belong to substances showing the widest differences in nature and behaviour, and which could not reasonably be classed together. Proteins may be suitably described as nitrogenous organic substances, always found in the colloid state, and which are broken up into amino-acids by boiling with acids or alkalies, or by the action of certain ferments or enzymes, *e.g.* trypsin. This breaking up is known as hydrolysis, and is of great importance. It forms part of the digestive processes, occurs in the liming and bating of hides, in the manufacture of glues and gelatines, and also in all putrefactions. On this account some explanation must be given, and first something must be said about acids and amino-acids.

Acids.—Almost all organic bodies possessing acidic properties (*i.e.* which can form salts containing metals) have in their molecules a hydroxyl ($-OH$) group. The hydrogen of this group under appropriate circumstances can be replaced by a metal to form a salt.

E.g. C_6H_5OH, phenol, and C_6H_5ONa, sodium phenate.
C_2H_5OH, alcohol, and C_2H_5ONa, sodium ethylate.
$CH_3 . CO . OH$, acetic acid, and $CH_3 . CO . ONa$, sodium acetate.

Typical acids, in which acidic properties are well defined, have the hydroxyl group attached to a carbon atom, to which is also linked a second oxygen atom, the whole forming what is called the carboxyl group:—



or $-COOH$.

In this way three of the four valencies of the carbon atom are involved, the fourth being used for a hydrogen atom or some monovalent group of atoms (monovalent radical). Examples of acids are:—

1. $H . COOH$, formic acid.
2. $CH_3 . CH_2 . COOH$, propionic acid.
3. $CH_3 . CH(OH) . COOH$, hydroxy-propionic or lactic acid.
4. $CH_3 . CH(NH_2)COOH$, amino-propionic acid or alanine.

It will be noticed that acids 2, 3, and 4 are constitutionally closely related. Lactic acid differs from propionic in having a hydroxyl group attached to the middle carbon atom in place of one of the hydrogen atoms. In alanine, the amino-group ($-NH_2$) plays the same part; compounds similar to alanine are called amino-acids, and form a numerous class, of which about eighteen can be found in the hydrolytic products of proteins. Indeed, these eighteen can be obtained from most single proteins, and the great majority in any case. The formulæ of some of the simpler amino-acids are as follows:—

Glycine or glycocoll, $CH_2(NH_2)COOH$, amino-acetic acid.

Tyrosine, $HO.C_6H_4.CH_2.CH(NH_2)COOH$, hydroxyphenyl-amino-propionic acid.

Glutamic acid, $HOOC.CH_2.CH_2.CH(NH_2)COOH$, amino-glutaric acid.

Lysine, $CH_2(NH_2)CH_2.CH_2.CH_2.CH(NH_2)COOH$, diamino-caproic acid.

In all amino-acids derived from proteins, one amino-group is attached to the carbon atom nearest to a carboxyl group. This applies to glutamic acid, which has two carboxyl groups, as well as to lysine, with two amino-groups.

Amino-acids differ in one very important respect from other acids, the difference being due to the nature of the amino-group. This group is basic. As a consequence, amino-acids can form salts not only with bases but with acids.

E.g. $CH_3.CH(NH_2)COOH + HCl \rightarrow CH_3.CH.NH_3Cl.COOH$.

Cp. $C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3Cl$, aniline hydrochloride.

$H.NH_2 + HCl \rightarrow H.NH_3Cl$, ammonium chloride.

In the presence of bases, therefore, amino-acids act as acids and form metallic salts; in the presence of acids, however, they act as bases and form hydrochlorides, etc. Tyrosine, for instance, is only soluble to a very slight extent in water, but dissolves readily in hydrochloric acid as hydrochloride and in alkali as tyrosinate. This behaviour is expressed in the word "amphoteric," a word implying the capacity of a substance to act as either acid or base according to circumstances. Proteins are also amphoteric by reason of the way in which they are built up of amino-acids. Gelatin, for instance, can form either hydrochloride or gelatinate.

Hydrolysis.—The term hydrolysis used in our definition of proteins still requires explanation. From the point of view of organic chemistry, we may look upon hydrolysis as the breaking up of a compound by the addition of the elements of water. Experimentally this is only occasionally accomplished by simple treatment with water. In nearly every case it is necessary to heat the substance with more or less dilute acid or alkali. An example or two will help here. Take the case of ethyl acetate. If this substance be boiled with water, the reaction

$$CH_3 . COOC_2H_5 + HO . H \rightarrow CH_3 . COOH + C_2H_5OH$$

will at first proceed in the direction indicated, but after a time an equilibrium is reached. If the complete hydrolysis of ethyl acetate is to be accomplished, acid or alkali must be used. Acid in sufficient strength, although it does not appear in the equation, will enable the reaction to be completed in a great number of cases, and all the acid originally used can be recovered at the end of the experiment. Alkali when used aids the hydrolysis by neutralising the acid product (forming sodium acetate in the example) until no more acid can be formed. Compounds which are hydrolysable in this way are those which we can imagine to have been formed by loss of water between two molecules. The formation of ethyl acetate from acetic acid and ethyl alcohol is such a case. Hydrolysis in the case of proteins is very often carried out by long boiling (six to twenty-four hours) with fairly strong acid (20 per cent. HCl or 30 per cent. H_2SO_4). More will be said on the experimental features in later sections of this chapter. For the present it must be understood that amino-acids form by far the greater part, often almost all, of the products of hydrolysis. It is therefore reasonable to assume that some mode of combination between amino-acids, a combination or "condensation" involving loss of water, is responsible for the typical protein molecule.

Constitution.—It is generally believed that the union of amino-acids to form peptides is the principal mode of combination in protein formation. There are, indeed, several ways in which the amino-acids could combine with loss of water, but since Hofmeister in 1902 surveyed the evidence there has been little doubt that loss of water between the amino-group of one acid and the carboxyl group in the other is the principal mode of union in building up a protein.

$$\mathrm{NH_2 \,.\, R \,.\, CO\boxed{OH+H} \,.\, NH \,.\, R_1COOH} \\ \rightarrow \mathrm{NH_2R \,.\, CO \,.\, NHR_1COOH + H_2O.}$$

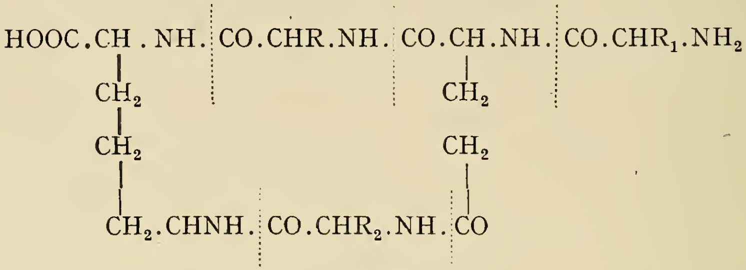
The body represented on the right-hand side of the equation is called a dipeptide. Tripeptides, tetrapeptides, etc., contain the appropriate number of amino-acid radicals. For it will be realised at once that theoretically there is no limit to the number of amino-acids that can be combined together to give one polypeptide. Experimentally the synthesis is difficult, but an oktadekapeptide containing eighteen radicals has been prepared, which proved to be remarkably like a natural protein. Assuming the polypeptide structure for proteins, hydrolysis is easily understood. Every $-\mathrm{CO \,.\, NH}-$ group is, by the addition of $\mathrm{HO \,.\, H}$, converted into an acid ($-\mathrm{COOH}$) and an amino-group ($-\mathrm{NH_2}$).

$$\mathrm{NH_2 \,.\, R \,.\, CO \,.\, NH \,.\, R_1 \,.\, CO \,.\, NH \,.\, R_2 \,.\, COOH + 2H_2O} \\ \rightarrow \mathrm{NH_2RCOOH + NH_2R_1COOH + NH_2R_2COOH.}$$

It is easy to see that the polypeptide structure gives the possibility of great variety and complexity in proteins. Plimmer states that there are 276 possible dipeptides. Possible tri- and tetrapeptides are far more numerous, as with increasing complexity the variations in arrangement of acid radicals which may occur increase out of all proportion to the number of radicals involved, according to the laws of permutations. If we consider three acid radicals, *a*, *b*, and *c*, and consider pentapeptides which they could form, we soon find that we could write down new ones apparently indefinitely:—

a-a-a-a-a	*b-a-a-a-a*	*c-a-a-a-a*
	a-b-a-a-a	*a-c-a-a-a*
	a-a-b-a-a	*a-a-c-a-a*, and so on.

Of course a polypeptide *a-b-c* is quite distinct from *b-a-c*. This complexity is made greater still by the formation of branched chains and ring structures, possibility of anhydride formation, etc., and the presence in many proteins of other groups not of a peptide character. Mucins, for example, contain carbohydrate.



The example is a hypothetical pentapeptide having a ring structure. The broken lines show where hydrolysis will take place. When it is remembered that eighteen or more amino-acids may be involved in a protein molecule, it is easy to see that only by the merest chance can a natural protein be synthesised, even if we assume that we know all about the type of structure. As a matter of fact, this assumption would be far from justifiable, for in any case the analysis of a protein does not show the *order* in which the amino-acids have been linked. As it is here that the greatest causes of variety lie, it would appear that what is needed most is some method of experiment allowing amino-acids to be split off one by one or in small groups, so that the order obtaining in the protein can be worked out.

It is possible for amino-acids to unite in other ways without loss of water between the molecules. As the amino-acids are both acids and bases, it is at least possible for them to combine with each other.

$$NH_2 . R . COOH + H_2N . R_1 . COOH \rightarrow NH_2R . COOH_3N . R_1COOH.$$

Cp. $CH_3 . COOH + H_2N . H \rightarrow CH_3 . COOH_3NH,$
ammonium acetate.

And as polypeptides always contain both free amino-groups and free carboxyl groups, then it is possible for polypeptides to combine with each other in the same way, even if the amino-acids within them have combined by loss of water. Bayliss has shown that in the case of amino-acids at least this salt formation is more than a theoretical possibility. He obtained indubitable evidence from conductivity measurements that combination occurred when diamino-propionic acid and glutamic acid were brought together. Thus, though there is no direct evidence on the point, proteins may consist of polypeptides of moderate complexity combined with each other to form salts.

Another possibility is that in proteins polypeptides are combined with each other through residual valencies in some such way as water of crystallisation is held by many inorganic salts. Here again the only experimental evidence concerns amino-acids. Pfeiffer and Modelski have obtained with amino-acids and certain metallic chlorides compounds of the type

$$CaCl_2(NH_2RCOOH)_4 \,.\, (H_2O)_n.$$

Here the amino-acids as wholes combine with a metallic salt as nucleus, and it is not difficult to imagine similar behaviour in the case of polypeptides. An interesting fact in this connection is that proteins are never quite free from small quantities of inorganic substances.

CLASSIFICATION

Some of the more important proteins are given in the following list:—

Albumins. Egg-albumin. Serum albumin.—The chief characteristics of these proteins is that they are coagulated by heat. They are precipitated from aqueous solution by full saturation with ammonium sulphate.

Globulins.—Ovoglobulin from egg-white. Precipitated by half saturation with ammonium sulphate. Coagulable by heat, insoluble in water, but soluble in dilute salt solutions.

Gliadins.—Wheat gliadin. Insoluble in water and absolute alcohol, but soluble in 50 to 70 per cent. alcohol.

Scleroproteins.—Collagen, gelatin, keratins, elastin. These proteins do not much resemble one another. They are usually insoluble in water. They form the skeletal structures of animals.

Phosphoproteins.—Casein. These contain phosphorus, probably in combination with one of the amino-acids.

Glucoproteins.—Mucins, in saliva and some tissues. These contain carbohydrate, which is split off on hydrolysis.

Chromoproteins.—Hæmoglobin, in blood.

Hydrolysis of Proteins

The course of hydrolysis, whether effected by acids, alkalies, or enzymes, may be roughly represented by the following scheme:—

Protein (collagen, casein, albumin, etc.)
↓
Metaprotein (Lieberkühn's jelly)
↓
Proteoses (gelatoses, albumoses)
↓
Peptones
↓
Simple Polypeptides (kyrins)
↓
Amino-acids.

The protein is broken up into simpler bodies, and these again into others, until amino-acids are produced, which of course cannot be further hydrolysed. Thus metaprotein is only a little less complex than the original protein, and retains many of its properties. Proteoses are formed by the hydrolysis of metaprotein, and so on. It must not be assumed that the whole of the original protein is converted into proteose before any peptone or amino-acid is formed. In some cases (*e.g.* hydrolysis of casein by trypsin) even amino-acid, the last product, is present from the very beginning of hydrolysis. Further, it must be understood that there is no sharp distinction between, say, albumoses and peptones, and that, on the other hand, different albumoses or different peptones may be present together amongst the products of hydrolysis of a single protein. The usual tests and methods of separation for the products of hydrolysis will now be given.

Metaproteins.—These are only familiar in the hydrolysis of albumins and globulins, and are prepared by the action of dilute (0·4 to 1·0 per cent.) acids and alkalies at moderate temperatures. As they are insoluble in water they are precipitated on neutralisation. Metaproteins are rendered insoluble in acid or alkali by boiling with water. They are distinguished from globulins by their insolubility in dilute solutions of neutral salts.

Proteoses are soluble in water, but completely precipitated by saturation with ammonium sulphate. They are, in fact, divided into two classes, primary and secondary, the former being completely precipitated by half saturation, the latter only by complete saturation with ammonium sulphate. There are also other distinctions.

	Primary Proteoses.	Secondary Proteoses.
Nitric acid . . .	Ppt.	No ppt.
Potassium ferrocyanide and acetic acid . .	Ppt.	No ppt.
Copper sulphate . .	Ppt.	No ppt.

Although secondary proteoses appear to approach the peptones in properties, they are not as a rule regarded as formed from primary proteoses by further hydrolysis. Both kinds of proteose are formed at the same time, roughly speaking, from the protein molecule.

Peptones are not precipitated by saturated ammonium sulphate. They retain, however, sufficient of the protein character to give precipitates with gallotannin and phosphotungstic acid. Peptones are very soluble in water, and give evidence of lower molecular weight, as they diffuse, though only slowly, through parchment paper. An important reaction for the purification of peptones is due to Siegfried. After secondary proteoses have been removed by saturation with ammonium sulphate (preferably in the presence of sulphuric acid), iron ammonium alum in saturated ammonium sulphate solution is added. Under these conditions peptones only, and no amino-acids, are precipitated. Pure peptone can be recovered from this precipitate, and is colourless and ash-free, in contrast to the discouraging brown masses obtained by the earlier workers. Siegfried takes the view that peptones are not so simple in constitution (mol. wt. 400–600) as is often supposed, and regards the evidence from freezing-point determinations as unsound. Instead of peptones being fairly simple polypeptides corresponding to the above molecular weights, they are, he considers, feebly bound compounds of such polypeptides, largely dissociated in water, especially in dilute solution. This would partly explain (1) the higher molecular weights found by freezing-point determinations when the peptone is dissolved in phenol, (2) the very great increase in molecular weight with increase in concentration. Siegfried has prepared bodies which he calls kyrins by further hydrolysis of peptones. For example, the peptone formed by the action of trypsin on gelatin was heated with 12·5 per cent. hydrochloric acid at 38° C. until the specific rotation of the solution assumed a constant value. The kyrin in solution proved to be decidedly basic in properties, yielded arginine, lysine, and glutamic acid in equimolecular proportions when fully hydrolysed, and in fact was shown by further work to be a tripeptide.

Polypeptides.—It is probably safe to assume that some simple polypeptides are formed in the ordinary course of hydrolysis, and that the more complex peptones are not split up directly into amino-acids. The work of Siegfried on the kyrins supports this view. There is, however, an important point to be mentioned, namely, that acids and enzymes are to some extent able to form peptides and other anhydrides from amino-acids. In the course of protein hydrolysis, therefore, where the various stages are not sharply defined, it is always possible that peptides present may have been formed from amino-acids resulting from the hydrolysis. The presence of peptides would then indicate a step back.

Amino-acids have been previously described, and are the end products in complete hydrolysis. It has already been stated, however, that amino-acids may be present in certain cases from the very commencement of the process.

General.—A large amount of the work done on products of partial hydrolysis has been with fibrin, albumin, or gelatin as original material, and it is doubtful whether the above classification could be easily or usefully applied in the case of every protein. In the case of keratin, for instance, hydrolysis has to be carried further than with gelatin before soluble products are obtained. Gelatin dissolves in cold lime water in a day or two, and the solution gives no precipitate on neutralisation. Keratin is acted upon much more slowly, and the solution obtained (*e.g.* a used lime liquor) invariably gives a precipitate when neutralised. Obviously in the latter case it is impossible to test the behaviour with ammonium sulphate solutions. In this connection it is interesting to notice the complexity of used tannery lime liquors. We have present proteoses, peptones, amino-acids, etc., derived from at least four different proteins. These substances are in the form of calcium salts. Further, since certain bacteria present have the power of acting upon and "deaminising" amino-acids, we have in lime liquors free ammonia, and also acids (as calcium salts) derived from amino-acids by loss of ammonia.

Acid Hydrolysis.—Protein is heated with five or six times its weight of concentrated hydrochloric acid or 25 to 30 per cent. sulphuric acid. Until the protein is quite dissolved, the heating should be carried out on the water-bath. The solution is afterwards boiled under a reflux condenser until hydrolysis is complete, *i.e.* until the biuret test (p. 140) fails. This often takes about six to twelve hours with hydrochloric and twelve to twenty-four hours with sulphuric acid, but may require two or three days. After hydrolysis, most of the acid is removed by distillation *in vacuo* (or by addition of baryta if sulphuric acid has been used), and a slightly acid liquor obtained containing some quantity of black insoluble matter or humin. After filtration and decolorisation the solution is exactly neutralised and evaporated to a small bulk. Tyrosine and cystine crystallise out. The diamino-acids (arginine, lysine, and histidine) are then precipitated by phosphotungstic acid, and can be separated from the precipitate. The filtrate contains monoamino-acids, which are converted into their ethyl esters, and separated by fractional distillation of the esters at very low pressures (0·5 to 10 mm.). This is the method elaborated by E. Fischer, which was the first step towards the complete analysis of proteins. Large numbers of quantitative hydrolyses have been carried out, and a few of the results are given below. The figures are from tables in Plimmer's book.

	Gelatin.	Elastin.	Keratin from Horse hair.	Keratin from Wool.	Casein.	Albumin from Blood.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Glycine . .	16·5	25·8	4·7	0·6	0	0
Alanine . .	0·8	6·6	1·5	4·4	0·9	2·7
Valine . .	1·0	1·0	0·9	2·8	1·0	—
Leucine . .	2·1	21·4	7·1	11·5	10·5	20·0
Isoleucine .	0	—	—	—	—	—
Phenylalanine	0·4	3·9	0	—	3·2	3·1
Tyrosine .	0	0·4	3·2	2·9	4·5	2·1
Serine . .	0·4	—	0·6	0·1	0·3	0·6
Cystine . .	0	—	8·0	7·3	0·1	2·5
Proline . .	7·7	1·7	3·4	4·4	3·1	1·0
Oxyproline .	3·0	—	—	—	0·3	—
Aspartic acid .	0·6	+	0·3	2·3	1·2	3·1
Glutamic acid	0·9	0·8	3·7	12·9	11·0	7·7
Tryptophane .	0	—	—	—	1·5	+
Arginine .	7·6	0·3	4·5	—	4·8	—
Lysine . .	2·8	—	1·1	—	5·8	—
Histidine .	0·4	—	0·6	—	2·6	—
Ammonia .	0·4	—	—	—	1·6	—
Total .	44·6	61·9	39·6	49·2	51·4	42·8

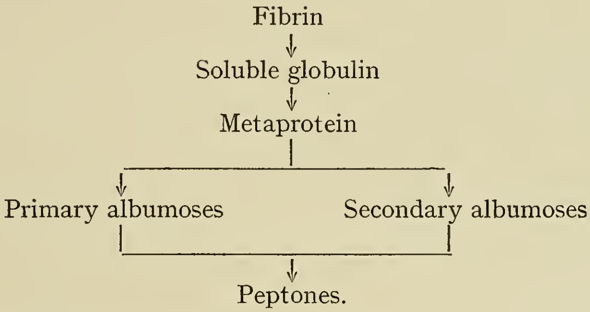
It will be noticed that in the above examples only about half the protein is accounted for. This is due in some cases to the fact that certain acids have not been estimated, but much more to the inevitable losses in the determination of monoamino-acids by Fischer's ester method. Recently Dakin has been able to make very great improvements in the estimation and separation of monoamino-acids. He extracts the aqueous solution with a non-miscible solvent, butyl alcohol, in which indeed the amino-acids are only very slightly soluble. But a continuous extraction process is used, similar to the extraction of tannin solutions by amyl acetate in qualitative analysis. Some of the amino-acids crystallise out from the alcohol during the extraction, others are not extracted. This method has been applied to the quantitative hydrolysis of gelatin, with the very interesting result that over 91 per cent. of the protein is now accounted for. Dakin's figures are given below, and should be compared with those of the older analysis (p. 135) which stood for many years as the best available:—

	Per cent.		Per cent.		Per cent.
Glycine .	. 25·5	Proline .	. 9·5	Arginine .	8·2
Alanine .	. 8·7	Oxyproline	. 14·1	Lysine .	5·9
Leucine	. 7·1	Aspartic acid	3·4	Ammonia .	0·4
Serine .	. 0·4	Glutamic acid	5·8		——
Phenylalanine	1·4	Histidine	. 0·9	Total	. 91·3
Tyrosine	. 0·01				

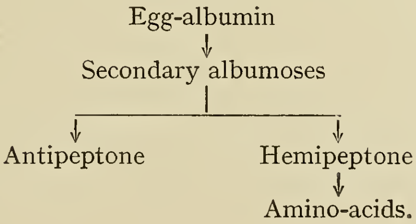
Alkaline Hydrolysis.—This is of very great interest in leather manufacture, but has received much less attention than acid hydrolysis. Results so far obtained go to show that the products by the two methods do not differ very much. Alkali seems to have the more powerful action. It has been stated that gelatin soon dissolves in cold lime water. In N/20 acid, however, hydrolysis is very slow at ordinary temperatures. In some cases resistant bodies formed in acid hydrolysis are much more quickly broken up by alkali. Abderhalden found that a resistant body obtained from silk could only be hydrolysed further by the use of alkali. Two other important points are: (1) cystine and arginine are decomposed by alkali, and (2) optically active amino-acids are rendered completely inactive.

A study of slow alkali hydrolysis at ordinary temperatures would be of very great interest to leather trades' chemists, especially with regard to the nature of the liming process. The great difficulties presented have no doubt deterred workers from taking up this subject.

Enzyme Hydrolysis.—This subject is of paramount importance to physiologists and biochemists, and has been the subject of much investigation. In leather manufacture enzyme hydrolysis occurs in both liming and bating, and must therefore receive some consideration. Several enzymes are capable of breaking up proteins, and amongst the most important are pepsin and trypsin. Such hydrolysis, however, is never complete. A resistant body named antipeptone is formed, which is never completely broken up even by the combined, or rather successive, action of different enzymes, though almost complete hydrolysis can be obtained in some cases if a sufficiently long time is allowed. Fischer and Abderhalden found that antipeptone contains all the phenylalanine and proline of the original protein. Of the two enzymes mentioned, trypsin effects the more complete hydrolysis, producing as a rule considerable quantities of amino-acids, whereas pepsin rarely carries hydrolysis past the peptone stage. The course of action of pepsin on fibrin is according to Cole as follows :—



Kühne's scheme for tryptic digestion is—



With regard to this latter scheme, it must be stated that the hemipeptone is a hypothetical substance and has never been isolated, and that some observers have found that nearly all the tyrosine is separated from casein in the first hour of tryptic digestion.

Enzyme hydrolysis is much affected by conditions of temperature, reaction, dilution, etc. Pepsin requires an acid medium, and is most effective in 0·2 per cent. hydrochloric acid, or at

$P_H = 1{\cdot}4$ about. Weaker acids must be used in appropriately higher concentrations. In alkaline solutions pepsin is very rapidly destroyed, especially on warming. It has been stated that peptic digestion produces nothing simpler than peptones and polypeptides. Indeed it would appear, according to Cole, that pepsin cannot break any peptide linkage since it does not hydrolyse any synthetic polypeptide. Trypsin acts best in alkaline solution at P_H about $8{\cdot}1$. It is not, however, destroyed by acids, but, according to some observers, is, in the absence of protein, even more stable in acid than in alkali. In carrying out hydrolyses by means of trypsin, care should be taken to have the reaction mixture alkaline to cresol red and acid to phenolphthalein. Trypsin acts on all soluble proteins, but not on all insoluble ones (*e.g.* collagen). It is sometimes necessary to give insoluble proteins a preliminary treatment with dilute acid or alkali or with pepsin. Hydrolysis will then in any case be more complete. It would appear that certain linkages in the protein molecule are opened up by pepsin, but not by trypsin. The products of tryptic digestion are simple polypeptides and amino-acids, the hydrolysis never being complete even after prolonged action. Trypsin is of great interest in leather manufacture, owing to its capacity for unhairing and bating skins. Probably the unhairing action depends on the digestion of the softer keratin of the epidermis, since the outer horny layer can often be removed bodily with the hair. The use of trypsin in bating will be discussed in a later chapter. All that need be said here is, that it appears to digest rapidly the elastin of the elastic fibres whilst having only a very slow action upon the collagen fibre

General Characters of the Proteins

Solubility, etc.—Some important proteins belonging to the class of scleroproteins appear to be quite insoluble in the unchanged condition, notably collagen, elastin, and the keratins. Acids and alkalies effect solution especially with the aid of heat, but hydrolysis has first taken place. Gelatin is insoluble in cold water, but always swells to several times its original volume. The swollen jelly on warming easily melts (at about 25° C.), giving a solution of gelatin. Very concentrated solutions can be prepared with hot water, but it should here be remarked that in no case should a gelatin solution be heated above 70° C. unless the hydrolysis which then begins is of no moment. Casein is insoluble in water, although particles suspended in water are able to redden blue litmus paper. It dissolves in alkali to form caseinate, and also in acid. Albumin swells somewhat, and dissolves in cold water. The mucins dissolve easily in dilute alkalies, and may be precipitated by neutralisation with acetic acid, though they are soluble in weak (0·1 per cent.) hydrochloric acid. Products of hydrolysis are in general soluble in water. Even insoluble proteins soon yield soluble products when hydrolysed. There are, however, exceptions, some of the amino-acids, for instance, not being very soluble.

Alcohol and organic liquids generally do not dissolve proteins. Gelatin, for instance, is readily thrown out of aqueous solution by addition of alcohol. On the other hand, some peptones and proteoses are soluble in alcohol. The gliadins behave remarkably in this respect. Wheat gliadin is perfectly insoluble in either water or pure alcohol, but dissolves in 70 to 80 per cent. alcohol. Urea solutions dissolve most proteins, probably by salt formation, since urea is a base. In a saturated solution of urea, gelatin will dissolve to the extent of 40 per cent. at room temperature. If the urea is removed by dialysis a jelly results.

Not much is known with regard to the degree of solubility of proteins in solutions of salts. Very considerable differences exist however, and afford means for the characterisation and separation of proteins. Globulins, for example, are insoluble in water, but soluble in dilute (10 per cent.) solutions of common salt. Higher concentrations cause precipitation (coagulation, "salting out"). Serum albumin begins to be precipitated from 1 per cent. solution by addition of 33 per cent. of ammonium sulphate, and is completely thrown out by 47 per cent. of the salt. Other salts have usually less precipitating power than ammonium sulphate, and are not so useful. Saturated magnesium sulphate is usually regarded as equivalent to half-saturated ammonium sulphate. For the details of the fractional salting out of proteins the reader is referred to the text-books.

Precipitation by Reagents.—Another mode of precipitation, in which the reagent chemically combines or reacts with the protein, is effected by various substances, notably the reagents used for precipitating alkaloids and the salts of heavy metals. The more important are given below.

(1) Mineral acids, *e.g.* nitric and metaphosphoric acids. Heller's test is performed by adding nitric acid slowly to the protein solution. A white ring appears at the surface of separation of the two fluids.

(2) The alkaloidal reagents include phosphotungstic, phosphomolybdic, ferrocyanic, picric and sulphosalicylic acids, and

tannin. The protein solution should be slightly acid before the reagent is added.

(3) The salts of heavy metals most often used are lead acetate, zinc and copper sulphates, and ferric chloride. The protein solution should be faintly alkaline. The precipitates formed are often soluble in acid or in excess of reagent.

The reactions under (2) require the protein to be in the acid or positively charged condition, as the reagents have a complex negative ion which is believed to be the effective agent in the reaction. The behaviour of tannin is explicable on similar grounds, as it is a negatively charged colloid in acid solution. In the reactions under (3) the protein is negative and the positive kation of the reagent is effective. A consideration of these reactions shows that substances such as copper sulphate and mercuric chloride can only be used under special conditions for the sterilisation of hides, since chemical combination may occur and unfavourably influence the subsequent processes of leather manufacture.

Colour Reactions.—Xanthoproteic Reaction.—This is carried out by the addition of strong nitric acid to the protein or its solution and then boiling. A yellow precipitate or solution is obtained, which becomes orange on the addition of alkali.

Millon's Reaction.—Millon's reagent is prepared by dissolving one part by weight of mercury in two parts of nitric acid (sp. gr. 1·42), warming if necessary towards the end of the reaction. The solution is then diluted with two volumes of water, allowed to settle, and filtered. When the reagent is added to a protein solution a whitish precipitate is formed, which becomes brick red on careful warming, or else dissolves, giving a red solution. This test only gives a positive result with proteins containing tyrosine. The xanthoproteic reaction is positive with proteins containing tyrosine, tryptophane or phenylalanine, *i.e.* the aromatic amino-acids.

Biuret Test.—According to Cole, 3 c.c. of protein solution (about 1 to 2 per cent.) is heated with 1 c.c. of 40 per cent. sodium hydroxide and one drop of 1 per cent. copper sulphate solution. A pink or violet colour is given not only with proteins but with proteoses and peptones.

Glyoxylic Reaction (Hopkins and Cole).—Protein solution is mixed with glyoxylic reagent, and an equal volume of concentrated sulphuric acid is poured down the side of the tube. A purple colour is seen at the surface of separation of the fluids, and with gentle shaking this colour spreads throughout the contents of the tube. The glyoxylic reagent is prepared by reducing oxalic acid with sodium amalgam or magnesium powder. The reaction is shown only by those proteins which contain the amino-acid tryptophane. Indeed the discovery of this substance by Hopkins and Cole was due to the study of the glyoxylic test.

Sulphur Reaction.—Protein is boiled with 40 per cent. caustic soda for a minute or two, and then a little lead acetate is added. A blackening results by the formation of lead sulphide from the sulphur of the protein.

Molisch's Reaction.—Protein solution is treated with a few drops of 1 per cent. solution of α-naphthol or of thymol in alcohol. After mixing, concentrated sulphuric acid is poured down the side of the test-tube. A violet colour appears at the surface of separation. This reaction is positive with proteins (*e.g.* mucins) which contain carbohydrate.

Crystallisation of Proteins.—Although crystalline bodies of a protein nature have been known for many years, it is only recently that the crystallisation of proteins has become at all generally practised. Aleurone grains were first noticed in 1850 in gluten, and occur in the seeds of many plants (*e.g.* hemp seed). Although they look like crystals, yet they behave differently from ordinary crystals. They swell, for instance, in water. In recent years, however, many proteins have been artificially crystallised, such as edestin, egg-albumin, gelatin, and hæmoglobin. The typical method is that of Hopkins and Pinkus for the crystallisation of egg-albumin. A solution of this protein half saturated with ammonium sulphate is prepared, and cautiously treated with 10 per cent. acetic acid until a permanent precipitate appears. A specified additional amount of acid is then added, which produces a heavier precipitate. The mixture is allowed to stand overnight, when the precipitate becomes crystalline. The protein can be recrystallised as often as desired. Other proteins are sometimes crystallised by means of alcohol. Von Weimarn, for instance, adds alcohol to an aqueous solution of gelatin until a slight permanent precipitate is formed. The mixture is then left in a desiccator containing strong sulphuric acid, by which means water is more rapidly removed than the alcohol. Crystallisation begins as the solution becomes richer in alcohol, and the insolubility of the gelatin increases. On the whole, however, it cannot be claimed that the crystallisation of proteins has at present any outstanding importance. Crystals obtained from ammonium sulphate solutions are always largely contaminated with the salt, and must be further purified by solution and dialysis. In any case, there is some doubt as to the identity of crystallised products and the original proteins. It should be mentioned that as a rule the crystals obtained are only recognisable as such under the microscope.

Coagulation by Heat.—Some proteins, *i.e.* albumins and globulins, are coagulated by heat. Egg-albumin coagulates when its solution is heated to about 55 to 60° C. This is of course a familiar occurrence seen every time an egg is cooked, but the nature of the change involved is quite obscure. There are, however, several points worthy of notice. In the first place, the coagulation differs from that produced by ammonium sulphate, etc., in being irreversible. Heat-coagulated egg-white cannot be brought back into solution. In the second place, the presence of alkali, acid, or of neutral salts (even in small quantities) is of great influence. Dialysed solutions often lose their coagulability owing to the presence of small quantities of alkali or acid, but long-continued dialysis will effect a recovery of this property. In the case of a dialysed solution no longer coagulable small quantities of neutral salt will, like further dialysis, render coagulation possible. The amounts required are much smaller in the case of calcium and magnesium salts than with alkali salts. Increase in the amount of salt raises at first the coagulation temperature sometimes by as much as 15 to 18° C., but may later cause a fall. It is therefore obvious that the coagulation temperature can only be characteristic of a protein under exactly defined circumstances. A non-coagulable protein may be freed, say, from albumin by heating the solution and filtering, but, as indicated above, such a process does not produce pure albumin.

Phosphorus and Sulphur Content.—Almost all proteins contain sulphur. The amount present is usually quite small, and varies very much in different proteins. Peptones are, as a rule, free from sulphur. One class of proteins, the keratins, is distinguished by comparatively high sulphur content (2 to 5 per cent.), few others containing so much as 2 per cent. Only one amino-acid, cystine, contains sulphur, and the amount of this element is often taken as a measure of the cystine content of a protein. This procedure is perhaps not free from objection.

A few proteins contain considerable amounts of phosphorus. Of these the best known is casein, which contains 0·85 per cent.

Distribution of Nitrogen in Proteins.—It has already been pointed out that the amount of nitrogen contained in a protein rarely varies very much. Nevertheless the distribution of the nitrogen, *i.e.* the amounts combined in certain groups of amino-acids, shows considerable variation, and is often useful in characterising proteins. A rapid method for the determination of the distribution was first worked out by

Hausmann, and the figures obtained are often referred to as "Hausmann numbers." The original procedure has been modified by several workers, notably Osborne, whose method is in outline as follows. One grm. of protein is completely hydrolysed, freed from most of the acid used, and subsequently distilled with magnesia. The ammonia liberated is equivalent to the " amide " nitrogen, which is believed to exist in the protein in $-CONH_2$ groups. The remaining solution is filtered. The residue is not only magnesia, but contains the black precipitate formed in hydrolysis. The whole residue after washing is analysed by Kjeldahl's method, and the result gives the " humin " nitrogen. The filtrate contains the monamino- and diamino-acids. The latter acids are with proper care precipitated by phosphotungstic acid, and the " diamino " nitrogen determined by analysis of the precipitate. The " monamino " nitrogen is calculated by subtracting the sum of the three quantities already determined from the total nitrogen of the original protein. In illustration of the results obtained, zein obtained from maize and conalbumin from egg-white may be compared. Each protein contains 16 per cent. of nitrogen. Of this amount, 18·4 per cent. in the case of zein and 7·51 per cent. in the case of conalbumin is amide nitrogen, 77·6 per cent. and 65·1 per cent. monamino nitrogen, 3·0 per cent. and 25·8 per cent. diamino nitrogen, and 1·0 per cent. and 1·7 per cent. humin nitrogen. This example clearly shows the usefulness of the method. A further separation of nitrogen into seven groups is often carried out. The method, however, is too long to be described here.

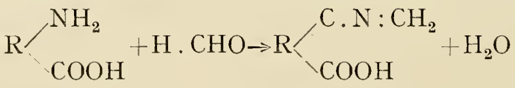
Action of Nitrous Acid on Proteins and Determination of free Amino-groups.—The well-known reaction between amino-groups and nitrous acid takes place, as would be expected, with proteins, since the presence of free amino-groups is *a priori* very probable. There is usually decided action accompanied by frothing and evolution of nitrogen. Amongst the most important of the early work was that carried out by Skraup, who prepared what he termed " desamido-proteins," and then investigated the products of hydrolysis of these bodies. The important conclusion to be drawn from this work is, that the diamino-acid lysine whilst combined in the protein molecule is acted upon and changed. All the other amino-acids were found in the hydrolysis products of the desamido-protein just as in the case of the original protein. Lysine, however, was never found. A second important fact due to Levites is that the amount of amide nitrogen (see above) in a protein is unaltered by the action of nitrous acid. The reaction was first studied quantitatively by Sachsse and Kormann in

1875, and much work has been done since by Brown and Millar, van Slyke, Fischer and Koelker, and others, and the estimation of nitrogen liberated by the action of nitrous acid on proteins is now a regular laboratory process described in text-books of physiological chemistry, etc. With a pure amino-acid the reaction is usually simple, as in the case of aspartic acid :

$$\begin{aligned}&\mathrm{HOOC\,.\,CH_2\,.\,CH(NH_2)COOH + HO\,.\,NO}\\ &\qquad\rightarrow \mathrm{HOOC\,.\,CH_2\,.\,CH(OH)\,.\,COOH + N_2 + H_2O.}\end{aligned}$$

Half the nitrogen evolved comes from the amino-acid. Anomalies occur, however, even with simple acids. Both glycine and cystine give a larger volume of gas than the simple equation accounts for. Fischer and Koelker found the reaction between polypeptides and nitrous acid to be somewhat indefinite and irregular, and that the nitrous acid reacts to some extent with the peptide (—CO . NH—) linkages. Nevertheless the interesting conclusion has been drawn, that in the case of proteins the nitrogen formed with nitrous acid comes entirely from one of the two amino-groups of lysine. A protein containing no lysine should therefore yield no nitrogen. This has been shown to be true in the case of zein, a protein obtained from maize. With other proteins it has been shown that the nitrogen obtained corresponds to half the lysine in the molecule. This work has received much support from the formaldehyde reaction which is described below. It is clear that during the hydrolysis of a protein the number of free amino-groups increases, and that an increasing proportion of the total nitrogen becomes reactive with nitrous acid. Edestin, for instance, contains 1·8 per cent. of its total nitrogen in free amino-groups, but when fully hydrolysed no less than 79 per cent. of the nitrogen is in that form. Clearly the nitrous-acid reaction gives valuable information as to the progress of hydrolysis.

Action of Formaldehyde on Amino-acids and Proteins.—Amino-acids are very weak acids, and it is not easy to titrate them with alkali in the ordinary way, owing to the hydrolysis of their sodium salts. If, however, they are allowed to react with formaldehyde, the basic character of the amino-group is destroyed, and very much stronger acids are produced, which can be easily titrated with alkali.



$$\mathrm{R}\begin{matrix}\diagup\mathrm{NH_2}\\ \diagdown\mathrm{COOH}\end{matrix} + \mathrm{H\,.\,CHO} \rightarrow \mathrm{R}\begin{matrix}\diagup\mathrm{C\,.\,N:CH_2}\\ \diagdown\mathrm{COOH}\end{matrix} + \mathrm{H_2O}$$

The formaldehyde used should be neutral to phenolphthalein, the indicator used. The acidity developed by the addition of formaldehyde is thus a measure of free amino and carboxyl groups, though in most cases no exact calculation can be made, since the various amino-acids are present in unknown proportions. Clearly, during the course of hydrolysis of a protein the formaldehyde titration will very markedly increase, just as the volume of nitrogen liberated by nitrous acid increases ; we should therefore have a means of following the course of hydrolysis and verifying the information given by the van Slyke nitrous-acid method. In practice the two methods do as a rule give parallel results, but there are one or two points about the formaldehyde titration which are causing it to lose favour. In the first place, formaldehyde does not react with some anhydrides of amino-acids. These bodies are certainly formed in hydrolysis, especially when prolonged, as has been shown by Fischer and Abderhalden. On this account alone, therefore, the formaldehyde titration will fail to give a correct indication of the course of hydrolysis. If amino-acids were being produced just as quickly as amino-acids already formed were condensing into anhydrides, then the titration would show no change. A second objection is that the reaction between histidine (an amino-acid) and formaldehyde is abnormal and irregular. Finally, the reaction in the case of any amino-acid is reversible, and hence in the titration an excess of alkali must be used, *e.g.* by titrating to a decided red colour with phenolphthalein. In spite of all this, however, it must be conceded that the method is certainly useful, one great advantage lying in the ease with which it can be carried out.

The action of formaldehyde on hide appears to be analogous to the action on amino-acids. A certain amount of acidity is always developed, due no doubt to the change in the amino-groups described above. The reversibility of the action on amino-acids, except in the presence of excess of alkali, is indicated in the case of proteins by two facts: (1) the formaldehyde can be easily split off quantitatively by distilling the compound in steam or by boiling with dilute (N/10) acid ; and (2) formaldehyde tannage is usually carried out in the presence of alkali. Qualitatively, proteins show considerable changes on treatment with formaldehyde. They are rendered resistant to pepsin, and probably to other enzymes, though a digestible protein is easily recovered by treatment with steam. Egg-white appears to lose its property of coagulating on heating. Soluble proteins often become insoluble. Gelatin, for instance, becomes a hard insoluble substance, and the setting point of gelatin jellies rises. If very dilute ($\frac{1}{2}$ per cent.) formaldehyde solutions are used, the reaction appears to require two or three weeks for completion. The time is much shorter when strong solutions are used. The amount of formaldehyde which combines with a given weight of protein has been investigated by Benedicenti, who added 4 c.c. of 2 per cent. formaldehyde solution to 10 c.c. of protein solution. His results, given by Schryver, are as follows :—

1 grm. gelatin	combines with	0·0135	grm. formaldehyde.
10 c.c. fresh egg-white	,, ,,	0·375	,, ,,
2 grm. powdered ,,	,, ,,	0·036	,, ,,
10 c.c. blood serum	,, ,,	0·315	,, ,,
3 grm. fibrin	,, ,,	0·0345	,, ,,
5 grm. casein	,, ,,	0·0294	,, ,,

These quantities will probably be only correct under certain experimental conditions, and too much importance should not be attached to them.

Action of Halogens, etc., on Proteins.—The action of halogens on proteins is complex, involving both oxidation and substitution. In spite of the very considerable amount of work which has been done on the subject, we have little or no clear understanding of the reactions involved. All proteins react directly with halogens, sometimes forming derivatives containing as much as 15 per cent. of halogen, as in some bromine compounds of egg-albumin, serum-globulin, proto- and deutero-albumose. These derivatives are readily soluble in alkaline solutions, from which they can be reprecipitated by acids. Some bromine derivatives are soluble in alcohol but not in the fat solvents. They can be salted out from alkaline solution by means of ammonium sulphate, but are not precipitated by the alkaloidal reagents ; they give the biuret reaction, but not the Millon and glyoxylic tests. At the same time as the halogen derivatives are formed, certain groups appear to be eliminated from the protein molecule. In the reaction products with iodine, ammonium iodide and iodate, iodoform, carbonic, formic, and acetic acids have been found, and it is supposed that these substances result from the scission of particular groups.

Collagen

Hide or skin consists of several proteins, namely, collagen forming the white fibres of the corium, keratins forming the epidermis, and hair or wool, mucins and albumins in small quantities in the corium, partly arising from blood and lymph, and also the elastin of the yellow elastic fibres. In the fresh hide collagen occurs in the swollen, hydrated condition, and although it is the only important hide constituent, very little is known of its chemical nature beyond what is deduced from the chemistry of the closely allied substance gelatin, which is described below. It is probable that there are several collagens derived from different hides and skins. The protein constituent of bone, which like hide yields gelatin on boiling with water, is also probably another collagen. There is, however, no real proof available, though analyses of purified corium from various sources show differences and support the above view. Von Schroeder and Paessler obtained the results given below :—

Source.	C.	H.	N.	O.
Ox, calf, horse, pig, camel, rhinoceros	50·2	6·4	17·8	25·4
Goat and deer	50·3	6·4	17·4	25·9
Sheep and dog	50·2	6·5	17·0	26·3
Cat	51·1	6·5	17·1	25·3

The figures for the nitrogen at least differ by more than the experimental error. The purification of the material is best effected by processes used in leather manufacture. After thorough cleansing the hide or skin is limed and unhaired, then washed, delimed, bated and scudded. By these means keratins, mucin, and elastin are removed, and what is left is regarded as collagen. On the laboratory scale it is desirable to treat the washed hide with trypsin in weakly alkaline solution in the presence of a little toluene to inhibit bacterial action. If the mixture is incubated at 37° C. the action of the trypsin is very rapid, and unhairing is soon accomplished. Elastin is also removed, according to recent work, as in the bating process. It is by this and similar methods that hide-powder (the purest form of collagen commercially obtainable) is prepared. The behaviour of collagen with trypsin is interesting. It resists the action of the enzyme unless it has been previously treated with either pepsin, acid, or alkali. This has been adduced as evidence that collagen has a ring, as distinct from an open-chain structure. The argument is, however, unconvincing, since many synthetic polypeptides have been prepared which cannot be hydrolysed by trypsin. The view that collagen is an anhydride of gelatin is an old one, held by Hofmeister and others, and is partly based on the uncertain evidence of elementary analysis. Some have considered that one molecule of gelatin loses one molecule of water, others that two molecules of gelatin lose one of water and thus become linked. Such a view has all the appearance of probability, and is supported firstly by the great resemblances in behaviour between gelatin and collagen, secondly by the ease with which collagen is converted into gelatin, and lastly by the fact that gelatin when heated to temperatures above 100° C. is gradually converted into an insoluble substance, which apart from lack of fibrous structure closely resembles collagen. The molecular weight of collagen is unknown, but certainly very high ; the combining weight of gelatin has been determined by Procter, and that of collagen may easily be the same (see Chapter X.). No boiling-point or osmotic-pressure determinations of the usual kind are possible, since collagen appears to be completely insoluble in water. Indeed, unless hydrolysis or other decomposition takes place, collagen will not dissolve in any reagent. Acids and alkalies swell collagen as they do gelatin, but no solution takes place unless the acid or alkali is fairly strong or assisted by heat or bacterial action. The view commonly held that hide-substance dissolves in 10 per cent. solutions of sodium chloride is probably erroneous. Many of the experiments quoted in its favour have been performed on hide incompletely purified, and in no case do the controls appear to have been sufficiently rigid. In other respects collagen behaves similarly to other proteins so far as its insolubility allows. It is acted upon by formaldehyde and the halogens, dehydrated or hardened by alcohol, strong solutions of ammonium sulphate, etc. The usual protein precipitants behave as tanning agents partly by chemical and partly by physical means. Hide gives all the colour reactions which can be carried out with solid protein, including the xanthoproteic and Millon tests. The first product of hydrolysis of collagen is gelatin, which is made by long boiling (many hours or even days) of purified hide, etc. Complete hydrolysis gives the amino-acids obtained from gelatin, enumerated in an earlier section of this chapter. The slow action or hydrolysis with cold dilute alkali or acid has not been studied from the chemical point of view. What is known with regard to gelatin will be described shortly, when it will be seen that one cannot take the identity of fresh and delimed hide for granted. The difference may be merely one of space arrangement of atoms within the molecule (*i.e.* stereo-chemical), but is probably real. The salt formation between collagen and acids or alkalies probably follows closely the behaviour of gelatin, and is largely a matter of physical chemistry (see Chapter X.). That real combination takes place is proved by the impossibility of freeing limed hide from lime by washing with water. The amount present can be reduced from 4 or 5 per cent. to 1·5 per cent., but no further.

GELATIN

Gelatin does not occur in hide, but is the first hydrolytic product of collagen. Its interest for leather trades' chemists is very great, since it has many points of resemblance with collagen, and has been the subject of much chemical investigation. The purest varieties occurring commercially are colourless and transparent, of horny toughness, and of specific gravity about 1·3. Gelatin has no definite melting point, but begins to soften with decomposition at about 140° C. In cold water, alcohol, ether, or hydrocarbons, gelatin is insoluble, but swells to a transparent jelly in the first named. This swelling is one of the most important properties of gelatin, and is especially marked in dilute acids and alkalies. A full discussion of the subject will be found in Chapter X. When the jelly is warmed it melts at temperatures from 30 to 40° C., and a solution of gelatin is obtained which sets again to a jelly on cooling if the concentration is above 1 per cent. Gelatin solutions should always be prepared by first swelling the gelatin, then pouring off the remaining water, adding further water as required, and finally melting by warming to a temperature not above 50° C. The last precaution is of importance if it is desired to dissolve the gelatin unchanged and avoid any further hydrolysis, since a solution heated to above 70° C. will never return to its original state. The setting and melting temperatures of the jelly will be found to be permanently lowered, owing to the increased peptone content. Methods for the examination of glues and gelatines will be found in the special text-books. The determination of the melting point of the jelly may be mentioned here, as it is of particular importance. An angular fragment of jelly should be put into a narrow glass tube attached to a thermometer, the whole in a beaker of water which is slowly heated until the jelly melts. Or the jelly may be allowed to set in an open capillary tube which is then treated as above, the temperature being noted when the water rises in the tube. The melting point varies very considerably with the quality of the gelatine, but is little affected by variations in concentration between 5 and 10 per cent. A 10 per cent. jelly of best hard gelatine melts at about 38° C.; glue may melt at a temperature as low as 15° C.

Purification.—In much chemical work the best commercial gelatines have been used without any further purification, and with no regard to the origin of the material, *i.e.* whether from hide or bones. It is obviously too much to expect that commercial gelatine can be a pure substance, nor can it be taken for granted that bone gelatine and skin gelatine are identical. The method of preparation by long boiling of hide makes purity in the chemical sense impossible, since gelatine formed at an early stage of the process will be subjected to the prolonged action of boiling water, and therefore notably hydrolysed. Actual examination proves that all commercial gelatines contain gelatoses and peptones, often in considerable quantities. Bogue has carried out analyses of some glues and gelatines with the following results:—

	Protein Nitrogen.	Proteose Nitrogen.	Peptone Nitrogen.	Amino-acid Nitrogen.
Russian isinglass .	91·0	4·4	4·5	0·1
Edible gelatine .	87·8	11·3	0·7	0·2
Hide glue . .	84·6	12·4	2·6	0·4
,, ,, . .	52·0	38·6	8·4	0·9
Bone glue . .	73·5	16·4	8·1	2·0
,, ,, . .	31·5	50·6	14·8	3·0
Peptone . .	0·0	33·2	48·5	18·3

Even the best French gelatine contains peptone. It is doubtful too whether the protein in commercial gelatine is a single individual. The presence of chondrin has often been suspected, but no strict examination has been made. The usual way of purifying gelatin has been to wash it for several days in running water, preferably after treatment with dilute acid. Inorganic impurities are thus largely removed by dialysis; some peptone will also disappear at the same time. Miss D. J. Lloyd has lately purified gelatin by soaking it in successive changes of acid of concentrations so chosen that the final product is at its isoelectric point (*i.e.* $P_H = 4·6$). So treated the gelatin is milk-white and not transparent, and the ash content is very low (0·1 per cent.). This method, however, does not appear finally to solve the problem. Dakin in the paper quoted above refers to the unsatisfactory nature of the present methods of purifying gelatin.

Coagulation by Reagents, and Optical Activity.—Gelatin is completely precipitated from solution by half-saturation with ammonium sulphate; indeed, from a preliminary experiment by the writer it appears to come down in slightly acid solution between 0·25 and 0·4 of complete saturation. It is also precipitated by magnesium sulphate, and also in the presence of a little acid by sodium chloride. The coagulum is of course heavily contaminated with the salt used, which can be removed only by dialysis. Alcohol acts in the same way, and the amount precipitated is often determined as an index to the quality of commercial gelatine. Twenty-five c.c. of 10 per cent. gelatin solution is treated with 75 c.c. of absolute alcohol. On stirring it becomes firmly attached to the rod and the sides of the beaker, where it may be washed with dilute alcohol, cold water, and finally dried and weighed. A French gelatine has yielded 98·6 per cent. of coagulum by this method, whilst glues may give no more than 60 per cent. Gelatin jellies shrink and harden by the same treatment. Alcohol will reduce a jelly to a horny mass by the withdrawal of water.

While discussing the physical behaviour of gelatin, it may be mentioned that its solutions are strongly lævorotatory to polarised light. At 30° C. the specific rotation is about −130°, but the temperature and reaction of the solution exert great influence on the value found. In common with other proteins, gelatin is racemised by the slow action of dilute alkali at moderate temperatures, *i.e.* N/2 or N/4 caustic soda at 30 to 40° C. In other words, the optical activity diminishes to a fraction of its original value. Dakin has explained this as due to a change in the mode of linkage at some $-CO.NH-$ groups. This change is known as the " keto-enol " transformation, and may be formulated thus :

Dakin is of the opinion that only those carbon atoms are unaffected which are contained in amino-acids at the ends of chains. Racemisation does not appear to be due to hydrolysis.

Reactions of Gelatin.—From the point of view of colour tests and precipitation reactions gelatin is hardly a typical protein. Its solutions fail to give the glyoxylic, Millon, and sulphur tests (in spite of the presence of sulphur), and produce only a slight xanthoproteic reaction. It follows that the amino-acids tryptophane, tyrosine, and cystine are absent, and that phenylalanine is only present in small quantity. This is borne out by the results of complete hydrolysis. Gelatin is precipitated by tannin and phosphotungstic acid, but not by normal lead acetate or ferrocyanic acid. This behaviour naturally suggests comparison with the albumoses.

The tannin-gelatin reaction is of such importance that some space must be devoted to it. All tannins precipitate gelatin even in very dilute solution, provided that excess of gelatin is avoided, as otherwise the precipitate is dissolved. The gelatin may behave here as a protective colloid. The most sensitive reaction is obtained with gallotannin, obtained from gall-nuts. Some substances such as alum, basic chrome liquor, and metaphosphoric acid intensify the reaction, others, positively charged colloids, retard it. In any case the reaction will only take place in an acid solution. If a series of trials with gallotannin and gelatin be made, beginning with acid solutions and adding small increasing quantities of alkali, the reaction will ultimately fail with rather surprising suddenness. There has been much debate as to the nature of the precipitate. Different workers have obtained the most widely varying results for its composition, and it was left to J. T. Wood to show that a precipitate of constant composition could only be obtained in the presence of a sufficient excess of tannin. If this excess were provided (6 parts tannin to 1 part gelatin), then 1 grm. of gelatin combined with 2·4 grm. of tannin, and variation in the concentration of the solutions was found to have very little effect. This result is sufficient to disprove any hypothesis based on so-called adsorption in which concentrations are the dominant factor and absolute amounts of no importance. The most probable explanation is that we have the mutual neutralisation of oppositely charged colloids, since when the reaction takes place, in acid solution only, we have the gelatin positively and the tannin negatively charged. This is followed by precipitation. In alkaline solution, when both colloids bear a negative charge and no neutralisation is possible, there is no precipitation. It will be noticed that this is strictly analogous to an ionic reaction. Instead of the mutual neutralisation of oppositely charged ions, the reaction is between large colloidal particles bearing charges probably derived from attached ions.

Various salts diminish the solubility of gelatin in water and raise the melting point of jellies. Such are alum, chrome alum, and basic chrome salts. Potassium dichromate behaves similarly when aided by the action of light. The dichromate is reduced and tans the gelatin. This behaviour is utilised in making cements. Formaldehyde also insolubilises gelatin. Other salts either raise or lower the melting point of gelatin jellies, but their effect is physical rather than chemical.

Hydrolysis.—The complete hydrolysis of gelatin has already been referred to and a list given of the products obtained. We ought to add a little about the phenomena of partial hydrolysis, though the work in this field has been very scanty. Well-defined peptones have, however, been isolated by Siegfried by his iron alum method after the action of pepsin or trypsin. These peptones have been subjected to further hydrolysis with interesting results. For instance, the peptone obtained by the action of trypsin was heated with 12·5 per cent. hydrochloric acid at 38° C. After 113 hours the optical rotation had fallen from −8·4° to −5·0°, and remained constant for 214 hours. From this solution a body was obtained which Siegfried calls a kyrin, and which, on hydrolysis, yielded only arginine, lysine, and glutamic acid. Further work on this body proved beyond reasonable doubt that it was an actual tripeptide, the elementary analysis giving figures almost exactly corresponding to theory. This result is an important contribution to knowledge of the structure of gelatin, seeing that it is less likely under the circumstances of the experiment that the tripeptide was formed from amino-acids previously split off.

ELASTIN, ETC.

Elastin.—This protein constitutes the yellow elastic fibres of the corium, and is of a stable character. It is scarcely possible to isolate it from hide, and our knowledge of elastin is mainly derived from that of the tendons and ligaments, particularly *ligamentum nuchæ*, the very strong and thick ligament in the neck of cattle, etc. This elastin is assumed without proof to be identical with that of the elastic fibres. In chemical properties elastin shows considerable similarity to keratin, being very resistant to boiling water and only slowly attacked by hot acids and alkalies. The products of complete hydrolysis have been given, and in this respect elastin does not resemble the keratins. The elastic fibres are apparently unable to combine with tannin. It has been stated recently by several writers that the elastic fibres tend to disappear in the bating process, being acted upon by the trypsin or other enzymes. This is a very attractive view of the bating process, and has been strongly supported by published photomicrographs. On the other hand, it has been objected that elastin from *ligamentum nuchæ* is resistant to trypsin. These facts are not inconsistent, since the identity of the two elastins is not certain, and also the elastic fibres before being bated are limed, which may make a very great difference.

Keratins.—The proteins of the hair and epidermis belong to the class of keratins. These substances are quite insoluble in water, though somewhat softened by it, and are very resistant to boiling water except under pressure. If heated with water at 160° C. for a long period the keratin is broken up, dissolving for the most part and evolving sulphuretted hydrogen. The softer keratins are hydrolysed fairly easily by caustic alkali, but hair and horn require strong hot solutions. The action of sodium sulphide is remarkable ; harder and softer keratins alike are easily attacked. As is well known, quite small quantities materially assist the unhairing action of lime-liquors. Keratins give all the protein reactions except when insolubility is an obstacle, since all the amino-acids giving the reactions are present, *e.g.* tyrosine, etc. The most striking feature in the chemistry of keratins is the high content of sulphur, due to the presence of large quantities of the amino-acid cystine. This amino-acid is decomposed by alkalies producing sulphide, which in the case of lime-liquors soon oxidises to sulphate and thiosulphate. A solution of keratin in alkali gives a precipitate (probably of proteoses) on acidification. This precipitate, which usually appears when a lime-liquor is neutralised, has been proposed as a filling material for leather, but without any very general success.

Mucins.—The mucins are conjugated proteins termed glucoproteins, since the protein is united with a carbohydrate group. Hence on hydrolysis with acids the solution obtained contains sugar and is able to reduce Fehling's solution. Mucins are easily soluble in dilute alkali, and are consequently removed from hide by the liming process. They can be precipitated by acetic acid from alkaline solution (provided that no hydrolysis has taken place), since they are insoluble in excess of acetic acid. The protein comes down as a stringy mass. All the characteristic protein reactions are given by mucins. One of the most characteristic features of mucins is the great viscosity of their solutions.

Casein.—This protein is never found in hide, but is interesting in leather manufacture, since it is a constituent of various finishes and cements. It is the principal protein of milk, belongs to the phosphoprotein class, is of a more pronounced acidic nature than most proteins forming fairly well-defined caseinates. In milk it probably exists as calcium caseinate, and is usually prepared from separated milk by acidification or treatment with rennet, when it precipitates at once. Casein dissolves in alkalis and less easily in acids. Few proteins have been so thoroughly investigated as casein, but the minor importance of the protein to the leather industry does not justify any discussion of the results here.

Albumins.—The albumins are soluble in water, dilute salt solutions, acids, and alkalies, and are the typical coagulating proteins. In neutral solution they are not precipitated by saturation with magnesium sulphate or half-saturation with ammonium sulphate, but in acid solution some precipitation occurs. Full saturation with ammonium sulphate causes complete precipitation. All the protein reactions are given by the albumins. Heat-coagulated albumin somewhat resembles keratin, being quite insoluble unless partially hydrolysed by acids or alkalies. Egg-white, the source of egg-albumin (ovalbumin), is a slightly alkaline fluid, containing about $\frac{1}{8}$ of solid matter and $\frac{7}{8}$ water. The protein is contained in membranes which are broken up by whisking. The albumin is here associated with a globulin, a coagulable protein which can be removed by half-saturation with ammonium sulphate. Serum or blood albumin is associated with a globulin in serum, the fluid left when the corpuscles are removed by centrifuging defibrinated blood. In preparing solutions of albumins care must be taken not to allow the temperature to reach the coagulation point.

Books for Reference

S. B. Schryver, *General Characters of the Proteins.* Longmans & Co.

R. H. A. Plimmer, *Chemical Constitution of the Proteins.* Parts I. and II. Longmans & Co.

S. W. Cole, *Practical Physiological Chemistry.* Heffer & Co., Cambridge.

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W. Pauli, *Kolloidchemie der Eiweisskörper.* Theodor Steinkopff, Dresden.

CHAPTER XII

SOAKING AND SOFTENING OF HIDES AND SKINS

As has been explained in the last chapter, hides and skins come into the hands of the tanner either uncured ("green"), as they are taken off the animal, preserved with salt or some other antiseptic, dried, or "dry-salted," in which both methods are combined. His object in each case is to remove blood and dirt, and to restore the hide to its soft and natural condition; but the treatment required varies much with the state of the hides.

Fresh hides merely require cleansing from blood and dirt. This is necessary because the blood causes bad colour from the iron contained in its hæmoglobin, and both blood, lymph, and adhering dung are sources of putrefaction, which ultimately attacks the grain and fibrous structure of the hide. Hence washed hides keep better than unwashed. Cold water is most desirable, as checking putrefaction. If the water is much over 10° C., or if it is charged with organic matter and ferment-germs, or if, as is too generally the case, the hides are in a partially putrid state when received, the time of soaking must be reduced as much as possible, and it may be necessary to sterilise the water with carbolic acid or creolin (pp. 21, 28). In such cases the use of a wash-wheel, or tumbler, is very desirable, rapidly cleansing the hides and removing adhering dung, which interferes with the liming, and is a serious cause of damaged grain. The American pattern of wash-wheel shown in fig. 25 is very suitable for the purpose. In no case is it desirable to allow green hides to lie for more than a few hours in water; and unwise treatment at this time is the cause of many troubles, which are only detected at later stages, and which are very difficult to trace to their source. "Weak grain," in which the grain-surface (p. 56) is destroyed, and which tans a whitish colour; "pricking," or perforation of the grain with small pinholes, which may go on to "pitting" with larger holes, and a general weakening of fibre, with softening and needless loss of weight, are among these results. An instructive instance may be quoted. A large tanner found that his curried leather was affected with small spots and rings of darker colour, which rendered it quite unfit for staining, and which reappeared even when the leather was buffed. When finished as black grain these spots had a tendency to " spue," or rise as little pimples of resinous matter. Before the leather was stuffed no defect was noticeable to the eye, but either then, or on stripping the grease by a solvent, they could be seen under the microscope as lighter patches of open and porous grain which absorbed more than their share of fat. During the tanning process they could hardly be detected, but in the first colouring they appeared for a few hours as blackish specks almost exactly like those caused by particles of iron or iron-rust. By careful observation they were traced back to the limes ; specimens of the limed hide were submitted to Director Eitner, who identified the defect as " *Stippen*," caused by a species of bacteria, which cannot subsist in limes, and which therefore must have been in the soaks. These, which had been somewhat neglected from pressure of work, were cleaned out and sterilised with creolin solution, and the mischief ceased. It is worth noting that the tanner dated the beginning of the trouble from the soaking of some " Spanish " horse-hides, which may have introduced the infection. Several very similar cases have come under the writer's notice.

It is not absolutely necessary to soak fresh hides or skins at all before liming, and where the water is scarce or unfavourable, or the skins tainted or " slipping " hair, it is best to pass straight into a weak lime. In this case the limes must be worked in shifts (see p. 179) and the whole of the oldest liquor run away and the hides rapidly changed into a fresh lime, or the limes will become so charged with organic matter and bacteria that the hides will cease to plump, and may even putrefy.

Salted hides and skins require more soaking and more thorough washing than fresh ones, as it is not only advisable to remove the salt, but to soften and plump the fibre which has been dehydrated and contracted by salting. If goods with salt in them are taken into limes they will not plump properly, and creases and wrinkles (drawn grain) are formed which no after-treatment will remove.[1] This is especially important in sole leather. In deciding on a method, we must bear in mind that salt is easily soluble, and diffuses rapidly into water or weaker solutions, but slowly into strong, and not at all into saturated ones. It may also be noted that though salt is not a true disinfectant (p. 21), salted hides

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[1] This opinion is generally held by tanners, and there is no doubt that salt does oppose the plumping of hide in caustic soda solutions, though not nearly so powerfully as in acids (as in the tan liquors). It is not improbable that the wrinkles and creases referred to are more due to want of sufficient swelling and softening in the water-pit than to the presence of the salt. Salt may increase swelling in unsharpened limes.

are much less prone to putrefaction than fresh ones, and therefore a longer soaking may be safely given.

These conditions point to the desirability of free exposure to water, attained by suspending, handling frequently, or tumbling, and repeated changes to remove the salt. The degree of removal of salt is easily determined by the estimation of Cl in the last wash-water (*L.I.L.B.*, p. 18). American tanners universally soak wet-salted hides three or four days with as many changes of water, and frequently finish by a few minutes in a wash-wheel. Any washing tumbler may be used ; but the cheap and simple construction of the American wash-wheel will be easily understood from fig. 25. The sides are open, so that hides can be put in or removed between the spokes. The rim of the wheel is generally perforated for the escape of water, which is supplied by a pipe passing through the axis ; and the wheel is often driven by a chain or rope round its circumference. No severe mechanical treatment, such as " stocking," is necessary or desirable for green or salted hides.

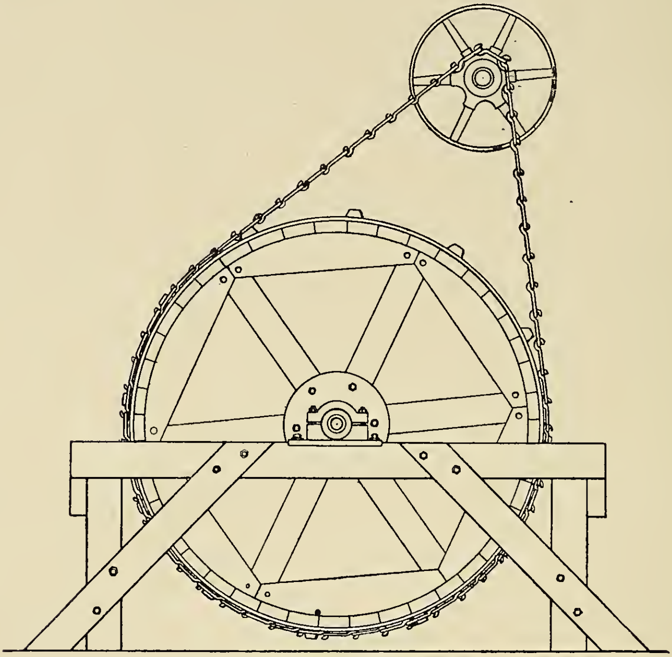

Fig. 25.—American Wash-wheel.

Dry and dry-salted hides require much longer soaking than wet-salted, the amount naturally depending on the thickness of the hide and the character of drying. Even thin skins when strongly dried require considerable time to soften and swell the fibres, although they soon become wet-through and flexible. Many different methods of soaking have been employed. Sometimes hides are suspended in running water ; sometimes laid in soaks which may be either renewed, or allowed to putrefy ; sometimes in water to which salt, borax, or carbolic acid has been added to prevent putrefaction ; and more recently weak solutions of caustic soda, sulphide of sodium, or sulphurous acid have been used with much success.

The first of these methods, were it desirable, is rarely possible in these days of River Pollution Acts ; of the others, it is difficult to say which is better, since the treatment to be adopted varies with the hardness of the hide and the temperature at which it has been dried. The great object is to thoroughly soften the hide without allowing putrefaction to injure it. As dried hides are often damaged already from this cause, either before drying, or from becoming moist and heated on shipboard, it is frequently no easy matter to accomplish this. The fresh hide, as has been seen, contains considerable portions of albumin, and if the hide is dried at a high temperature, this may become wholly or partially coagulated and insoluble. The gelatinous fibre and the coriin (if indeed the latter exists ready formed in the fresh hide) do not coagulate by heat, but also become less readily soluble. Gelatin dried at 130° C. can only be redissolved by acids, or water at 120° C. Eitner [1] experimented with pieces of green calf-skin of equal thickness, which were dried at different temperatures, with results given in the following table :—

Sample.	Temperature of Drying.	Remarks.	Time of Softening in Water.	Remarks.	Dissolved by Salt Solution.
I.	15° C.	*In vacuo*	24 hours	Without mechanical work	1·68%
II.	22° C.	In sun	2 days		1·62%
III.	35° C.	In drying-closet	5 ,,	Twice worked	0·15%
IV.	60° C.	,,	Refused to soften sufficiently for tanning.		traces

Hence it is evident that, for hides dried at low temperatures, short soaking in fresh and cold water is sufficient, and, except in

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[1] Gerber, 1880, p. 112.

warm weather, there would be little danger of putrefaction. With harder drying longer time is required, and more vigorous measures may be necessary. A well-known tanner recommended a brine of 30° to 35° barkometer (sp. gr. 1·035, or about 5 per cent. of NaCl). This has a double action, not only preserving from putrefaction, but dissolving a portion of the hide-substance, which is undoubtedly a loss to the tanner, though it is questionable if there is any process which will soften overdried hides without loss of weight ; since even prolonged soaking in cold water at a temperature which is too low to allow of putrefaction taking place will dissolve a serious amount of the hide-constituents. Chlorides, however, do not seem well adapted for the purpose in view, from their weak antiseptic power and tendency to prevent swelling. Jackson Schulz advised the use of water at 80° F. for soaking during the winter months. Water containing a small quantity (0·1 per cent.) of carbolic acid has been recommended for the purpose, and will prevent putrefaction, while it has no solvent power on the hide, but, on the contrary, tends to coagulate and render insoluble albuminous matters. Borax has been proposed for the same purpose, and, in 1 per cent. solution, certainly prevents putrefaction, and has considerable softening power, but is far too costly. Other methods of chemical softening are described on p. 161.

For some descriptions of hides, and notably for India kips, putrid soaks were formerly much employed, the putrefactive action softening and rendering soluble the hardened tissue. In India the native tanners soften their hides in very few hours by plunging them in putrid pools, into which every description of tannery refuse is allowed to run. Putrefactive processes, however, are always dangerous, as the action, through changes of temperature, or variation in the previous state of the liquor, is apt to be irregular, and either to attack one portion of the hide before another, or to proceed faster than was expected. Hides are also frequently more or less damaged by putrefaction and heating during the process of cure, and these damages are accentuated in a putrid soak. Hence hides in the soaks require constant and careful watching, and the goods must be withdrawn as soon as they are thoroughly softened, for the putrefaction is constantly destroying as well as softening the hides. It is possible that putrefactive softening is less injurious to kips, and such goods as are intended for upper leather, than to those for sole purposes, as it is generally considered necessary in the former case that a good deal of the albumin and interfibrillary matter be removed, and that the fibre be well divided into its constituent fibrils for the sake of softness and pliability; and thus the putrid soak, if acting rightly, accomplishes part of the work which would afterwards have to be done by the lime and the bate, as the actual fibre of the hide seems less readily putrescible than the softer cementing substance.

Putrefaction is caused, as we have seen, by a great variety of living organisms, each of which has its own special products and modes of action. It is quite possible that, if we knew what precise form of putrefaction was most advantageous, we might by appropriate conditions be able to encourage it, to the exclusion of others, and obtain better results than at present. Putrid soaks (in the old sense) are, however, disused in the present day by all enlightened tanners, as it is recognised that the risks outbalance the advantages, and when dry-salted hides are worked, the soluble salts of the cure accumulate in the soaks to an injurious extent. The modern method, where no chemicals are used, is to give one fresh water at least to each pack of hides or skins. Even in this case considerable putrefaction takes place where the soaking occupies seven to fourteen days, as is the case with kips and hides, and there is no doubt that the use of chemical and antiseptic methods of soaking will ultimately be generally adopted, both on technical and sanitary grounds.

The use of dilute acids for softening has much to recommend it, their power of causing the fibre to swell and absorb water being at least equal to that of the alkalies, while few, if any, putrefactive bacteria can thrive in an acid liquid. Very dilute sulphuric acid has been used with success to dissolve the alkaline "plaster" of East India kips (p. 39). It has considerable disinfectant power (p. 23), but its action on the hide-fibre is undesirably strong.

Sulphurous acid is much more suitable. Its use for this purpose was patented by Maynard, along with a number of other possible uses, but the patent has long lapsed, and he did not seem to have succeeded in introducing it into practice. Experiments at the Yorkshire College (now Leeds University), and also at a tannery on a manufacturing scale, have shown that the method is capable of excellent results. The hides are soaked for twenty-four to forty-eight hours in a solution of sulphurous acid containing about 2 per cent. of SO_2 (for manufacture, compare p. 24; for testing, *L.I.L.B.*, pp. 16, 37), and are then transferred to water, where they swell freely to their full thickness. They may be either limed at once, or first neutralised with dilute caustic soda, ammonia, or sulphide of sodium, which, for dressing leather, is perhaps desirable. No putrefaction takes place, even if they are retained for a considerable time in water, and the acid has little or no solvent effect on the hide-fibre, the strength of which is well preserved. The liming, however, must either be conducted with the aid of sodium sulphide or in old limes, since the sterile condition of the hides renders liming in fresh lime very slow (*cp.* p. 183). For experimental purposes a ½ per cent. solution of Boakes' "metabisulphite of soda" may be used, to which ¼ per cent. of concentrated sulphuric acid previously diluted with water is gradually added during the soaking, the hides being first withdrawn. For regular work it will be found much cheaper to manufacture the acid on the spot by burning sulphur.

The use of solutions of caustic soda (1 to 2 parts per 1000), or of sodium sulphide (1½ to 5 parts per 1000) as suggested by Eitner, seems at present likely to supersede all other methods of softening from their simplicity and safety. Twenty-four to forty-eight hours in either of these solutions, which may if necessary be followed by a short soak in plain water, seem sufficient to soften either kips or hides. Experiments at Leeds University have shown that solutions of this strength have little or no solvent action on the hide-fibre, but promote its swelling in water so effectively that no mechanical softening is needed (though a slight drumming is advantageous), while putrefaction is almost entirely prevented, so that the solution may be repeatedly used if kept up to its original strength, which is easily determined with standard acid and phenolphthalein (see *L.I.L.B.*, p. 17). Neither caustic soda nor sodium sulphide have any injurious effect on liming, though it may prove somewhat slower than with the older methods, where the epidermis was partially destroyed by the action of putrid ferments. The dilute solutions used are not only less injurious to the hide than those of greater strength, but they are also more effective in softening. Eitner (*Gerber*, 1899, p. 584) states that when using a solution of caustic soda of 1 part in 1000 strength, the time required to soften some hides was only two days, as against three days for a sodium sulphide liquor and four days for pure water, and that with the soda solution only about 0·6 per cent. of the hide-substance of the skin was dissolved out, whilst when sodium sulphide was used it was 0·7 per cent., and with pure water alone no less than 1·9 per cent. was lost by solution.

The use of moderately warm water (40° C.) in a drum is quite successful in rapidly softening sound hides after they have previously been soaked for some days in cold water; but if they are tainted in the cure, it is very apt to intensify the mischief. Hides which have partially putrefied internally, or which have been exposed to a hot sun while the interior is still moist, are very apt to appear sound while dry, but to blister or go to pieces from the destruction of the internal fibres as soon as they are limed, and this in spite of even the most careful treatment. For tainted hides, caustic soda is probably preferable to sodium sulphide.

Many chemicals have been patented for softening hides. Sulphide of arsenic is said to be in use, and if dissolved in caustic soda solution would differ little in its effect from ordinary sulphide of sodium. Saltpetre has also been employed, but its effect, if any, was probably merely antiseptic. Ordinary sodium carbonate has been used, but is less effective than caustic soda, and must be used in stronger solution. Gas liquor and mixtures of this with tar and water were patented by Barron, and probably the first would soften by virtue of its ammonia and sulphides, while tar contains carbolic acid. Probably the most absurd mixture of all was patented by Berry, which consisted of ½ bucket of slaked lime, ½ bucket of wood-ashes, 12 lbs. of potash, 5 lbs. of oil of vitriol, and 4 lbs. of spirit of salt !

Beside merely soaking the hides, it is sometimes necessary to work them mechanically to promote their softening ; this was formerly accomplished by " breaking over " the hides on the beam with a blunt knife. This process is still in use for skins of many sorts, but for the heavier classes of leather was usually superseded or supplemented by the use of " stocks," or drums. The former consist of a wooden or metallic box, of peculiar shape, wherein work two very heavy hammers, raised alternately by pins or cams on a wheel, and let fall upon the hides, which they force up against the curved end of the box with a sort of kneading action. The ordinary form of this machine is shown in fig. 26. A more modern form, which seems to possess some advantages, is the American " double-shover," or " hide-mill," seen in fig. 27. " Crank stocks," similar in form to the faller stocks, but driven by cranks, are sometimes used for softening, but are better adapted to lighter uses.

The number of hides which can be stocked at once naturally varies with the size of both hides and stocks, but should be such that the hides work regularly and steadily over and over. The whole number should not be put in at once, but should be added one after another, as they get into regular work. The duration of stocking is ten to thirty minutes, according to the condition and character of the hides. Hides should not be stocked until they are so far softened that they can be doubled sharply without breaking or straining the fibre. After stocking, they must be soaked again for a short time, and then be brought into an old lime. A small quantity of sodium sulphide added to the soaks or in the stocks has been recommended as of great value in softening obstinate hides, and probably with justice, from its well-known softening action upon cellular and horny tissues.

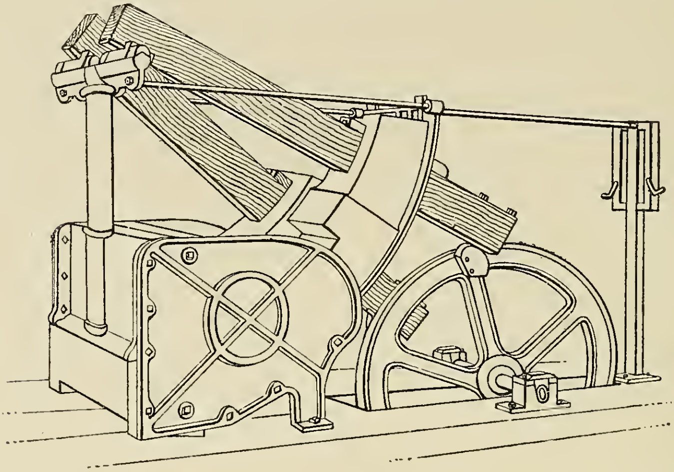

Fig. 26.—Faller Stocks.

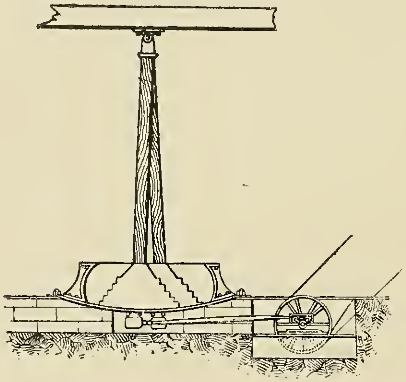

Fig. 27.—American Hide-mill.

Tumbler drums of various forms may also be used with good effect for softening purposes, especially for skins, and are much less detrimental than stocking, both as regards the weight and quality of the goods.

For sole leather, and even for kips, the use of stocks has in recent years been entirely discarded by many of the more advanced tanners. If mechanical work is required at all the drum is preferred, and is sometimes employed after a few days' liming, the goods being first merely softened in fresh water. The use of caustic soda, sodium sulphide, or sulphurous acid usually renders mechanical softening unnecessary.

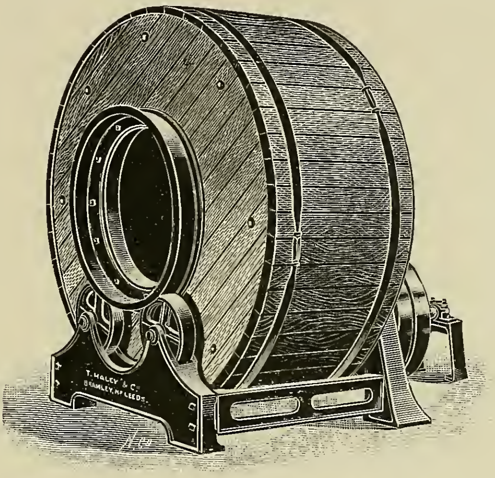

Fig. 28.—Drum for Washing or Tanning.

The drums employed are in principle like a barrel-churn, and are large cylindrical wooden chambers 6 to 12 feet in diameter, and fitted inside either with shelves like the floats of a water-wheel, or with rounded pegs on which the hides fall. The American wash-wheel figured on p. 158 is a machine of this kind, and one of a more elaborate description is shown in fig. 28. Drums are not only used for softening, but for tanning, dyeing, and many other purposes in leather manufacture. It is advantageous to be able to reverse the direction of their rotation to prevent the rolling up of the hides.

CHAPTER XIII

DEPILATION

After the softening and cleansing of the hide or skin is completed, and before proceeding to tan it, it is usually necessary to remove the hair or wool. The earliest method of accomplishing this was by means of incipient putrefaction, which attacks in the first instance the soft mucous matter of the epidermis, and thus loosens the hair without materially injuring the true skin. This loosening of the hair often takes place accidentally in hides which have been kept too long without salting, and is known as "slipping," and is apt to be accompanied by some degree of injury to the grain. The old method of loosening the hair by putrefaction, or, as it is generally called, "sweating," was to lay the hides in piles, usually in some warm and damp place. Occasionally a slight preliminary salting was given to prevent too much putrefaction of the hide. The action in this case, however, was very irregular, and it has been quite abandoned in all civilised countries.

A method which is still used to some extent in America, principally on dry hides, is to hang the hides in a closed chamber, generally called a "sweat-pit," fig. 29, but usually constructed above the ground-level, and protected from sudden changes of temperature by double walls, or by mounds of earth. The hides are hung in the sweat-pit, in small chambers each capable of holding 50 or 100 hides. The temperature is kept at about 15° to 20° C., the air being warmed, if necessary, by the admission of steam below a perforated floor, or cooled by a shower of water from sprinklers, so arranged as not to play directly on the skins, and is thus always kept saturated with moisture. Little if any ventilation is allowed, and a large quantity of ammonia is given off from the decomposition of the organic matter, and no doubt contributes to the solution of the epidermis and the loosening of the hair, as the writer has found that ammoniacal vapours alone very speedily produce this effect. It may here be suggested that the use of ammoniacal gas for sheep-skins deserves practical trial, as the loosening of the wool is very rapid, and no injury is done either to it or to the pelt. The ammonia could be recovered by passing the air of the chamber through an acid "scrubber," or probably transferred to a second chamber by displacement with cold air, as ammonia gas is lighter than air and would float on colder air admitted at the bottom. Ammonia is also formed during the process.

After four to six days of this treatment the hair is sufficiently loosened to be removed by working the skin over the beam with a blunt knife, or by means of the stocks or hide-mill (see p. 164). Great care and watchfulness are required to avoid injury to the grain by putrefaction.

The hide is in a slimy and completely flaccid and "fallen" condition, and some trouble is occasioned by the hair being worked into the flesh by the hide-mill, to obviate which a slight liming is frequently given after the sweating. Hides which have been unhaired in this way require to be swollen by acid in the liquors in order to produce a satisfactory sole leather, as the sweating process does not swell or split up the fibres.

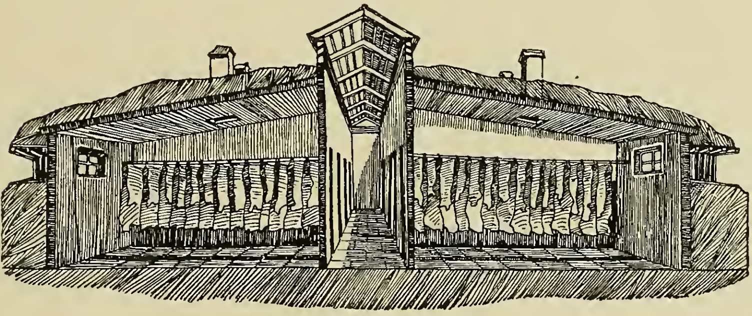

FIG. 29.—Sweat-pit.

In some European tanneries a similar process, but at a higher temperature, is employed, and it is also largely used for sheepskins under the name of "staling," but in this case is sometimes conducted in a very rude and primitive manner, and frequently with the result of considerable injury to the pelt. This injury is not always bacterial. A case is described by P. Hampshire[1] in which great destruction to pelts was caused by nematode worms. The process is adopted because the wool on these skins is of greater value than the pelt, and is less injured than by liming, but is being largely superseded by painting with sulphide mixtures.

The great objection to the sweating process, however carefully conducted, is the liability of putrefaction to attack the skin

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[1] *J.S.L.T.C.*, 1921, 5, p. 20.

itself, causing " weak grain." Its most advantageous use is for sole leather, as, although the solution of the hide-substance may not be very much less than in the case of liming, the dissolved matter remains in the hide instead of being washed out, and being fixed by the tannin, contributes to the solidity of the leather.

In England, lime is the agent almost universally employed for unhairing (now almost invariably with the addition of alkaline sulphides), though every tanner admits its deficiencies and disadvantages. It is hard, however, to recommend a substitute which is free from the same or greater evils, and lime has one or two valuable qualities which will make it very difficult to supersede. One of these is that, though it inevitably causes loss of substance and weight, it is also impossible, with any reasonable care, totally to destroy a pack of hides by its use; which is by no means the case with some of its rivals. Another advantage is that, owing to the very limited solubility of lime in water, it is of comparatively small consequence whether much or little is used; and even if the hides are left in a few days longer than necessary, the mischief, though certain, is only to be detected by careful and accurate observation. With all other methods, exact time and quantity are of primary importance, and it is not easy to get ordinary workmen to pay the necessary attention to such details. Again, the qualities of lime, its virtues and failings, have been matter of experience for hundreds of years, and so far as such experience can teach, we know exactly how to deal with it. A new method, on the other hand, brings new and unlooked-for difficulties, and often requires changes in other parts of the process, as well as in the mere unhairing, to make it successful. As our knowledge of the chemical and physical changes involved becomes greater, we may look to overcoming these obstacles more readily.

The universal source of lime is chalk or limestone, which consists of calcium carbonate, and from which the carbon dioxide is driven off by burning in a kiln. Many limestones, however, are far from being pure calcium carbonate, but contain large proportions of magnesia, iron, and alumina, the latter perhaps originally deposited in the form of clay with the sediment from which the stone was formed. Such clay limestones when burnt yield natural cements, like oolite and other " hydraulic " limes, which are capable of setting even under water. The presence of magnesia and clay is injurious, not only by diminishing the amount of lime present, but by making the lime much more difficult to slake; and iron oxide, though quite insoluble, may become mechanically fixed in the grain of the hide, and may be the cause of subsequent stains. The burning of lime in the kiln is probably not quite so simple an operation as the equations of the text-books would suggest. By mere heating the carbonate can, it is true, be decomposed, but to do this completely a good white heat is required, which is rarely attained in practical burning, and it is probable that at least a part of the carbon dioxide present is reduced to carbon monoxide by the combustible fuel-gases, and so separated from the lime, for which it has no affinity. Carbon monoxide is the cause of the intensely poisonous character of lime-kiln gases, the pure dioxide being irrespirable, but not strictly poisonous.

Quicklime, CaO, on coming in contact with water, combines with it with the evolution of considerable heat, becoming slaked or converted into hydrate, $Ca(OH)_2$. This change takes place rapidly and easily when the lime is light and porous, such as is obtained by the burning of chalk or good limestone at a low temperature ; but if it has been too intensely heated or "overburnt," or contains silicates or other salts which fuse at the temperature of the kiln, a compact lime is formed which slakes with difficulty and extreme slowness, thus being lost to the tanner, or leading to the still more serious result of burning holes in the hides by the heat produced by slaking in contact with them. It is stated by Le Chatelier[1] that for dense limes twenty-four to forty-eight hours is frequently required for complete slaking in the cold, while magnesia is still more obstinate, months being sometimes necessary for the complete hydration of hard-burnt samples ; and mixtures of lime and magnesia are intermediate in their character. Slaking is greatly assisted by heat, even heavily burnt magnesia being hydrated in about six hours at 100° C. Slaking is also much more rapid in a dilute solution (2 per cent.) of calcium or magnesium chloride. From these facts it is easy to deduce the reason why a suitable quantity of water, neither too much nor too little, is desirable for the rapid and effectual slaking of lime. If too little is used, the lime is only partially slaked, and it is not easy for further portions of water to gain access to the interior of the powdery mass. On the other hand, if it is "drowned" by excess, the temperature is lowered, the process goes on slowly, and the mass does not readily fall into powder, and so fails to be utilised in the liming process. Of all methods of slaking lime, the ordinary one of tipping it direct into the lime-pits is perhaps the most irrational,

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[1] *Bull. de la Soc. d'Encouragement*, 1895, x. pp. 52–62 ; *Journ. Soc. Chem. Ind.*, 1895, p. 575.

leading to the formation of unslaked lumps which may burn the hides, and which, together with stones and dirt, rapidly choke the pits with useless matter. The best process is that adopted by builders and in many Continental yards, in which a large quantity of lime is slaked in a shallow tank by throwing on it sufficient water to thoroughly wet it, and after allowing it to heat and fall for twenty-four hours, adding enough water to convert it into a stiff paste. In this form it may be kept for months without material deterioration. When required for use, a suitable quantity of the paste is dug out, and well stirred with water in a tub or tank before running into the pit, when the stones and sand remain in the tank. In this way all nuisance from dust is also avoided. If lime is stored unslaked, it gradually absorbs moisture from the air, falling, and soon becoming dusty and difficult to slake completely, while the traces of carbon dioxide in the air gradually convert it into useless carbonate.

The solubility of lime in water is very limited, and the figures determined by different chemists do not agree very satisfactorily. The following table gives the result of determinations made by Mr A. Guthrie in the Author's laboratory, and is probably one of the most accurate :[1]—

100 c.c. of	saturated lime water at	5° C.	contain	0·1350	grm. of CaO.
,,	,,	10°	,,	0·1342	,,
,,	,,	15°	,,	0·1320	,,
,,	,,	20°	,,	0·1293	,,
,,	,,	25°	,,	0·1254	,,
,,	,,	30°	,,	0·1219	,,
,,	,,	35°	,,	0·1161	,,
,,	,,	40°	,,	0·1119	,,
,,	,,	50°	,,	0·0981	,,
,,	,,	60°	,,	0·0879	,,
,,	,,	70°	,,	0·0781	,,
,,	,,	80°	,,	0·0740	,,
,,	,,	90°	,,	0·0696	,,
,,	,,	100°	,,	0·0597	,,

It will be noticed that unlike that of most substances, the solubility of lime in water diminishes as the temperature is raised. It is therefore necessary in employing lime-water as a standard solution to take care that it is saturated at a constant temperature. The results given in the above table are those from pure marble lime. Where the ordinary impure limes from limestone are employed, a somewhat stronger lime-water is often

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[1] *Journ. Soc. Chem. Ind.*, 1901, p. 224.

obtained. This is difficult to explain, but possibly some double hydrate of lime and magnesia is formed which is more soluble than either hydrate alone. It is also possible that a lime may contain traces of soda or potash, or of baryta or strontia, which are more soluble than lime itself. These facts harmonise with the old belief of tanners that chalk-lime is milder in its action on skin than that made from less pure limestones. The solubility of any given lime is easily determined by adding it in excess to water in a stoppered flask, and shaking frequently until a solution of constant strength is obtained. A known volume of this solution (which must be clear and free from undissolved lime) is then titrated with N/10 hydrochloric acid, using phenolphthalein as the indicator.

Saturated lime-water may be conveniently used as an alkaline standard solution for many purposes, and if kept on excess of lime, is always caustic, and varies very little in strength at ordinary laboratory temperatures. The solution is nearly 1/20 normal, but for accurate work its strength should be exactly determined with N/10 acid. One liter of pure lime-water at 15° C. should require 471·4 c.c. of N/10 acid for neutralisation. If a lime-water made by shaking good excess of lime with distilled water at 15° C. requires more than this amount of acid, it may be presumed that some other soluble base is present. Of course the amount found will in this case be dependent on the amount of lime used in excess.

Lime is much more soluble in sugar solutions than in water. Such solutions have been used as standard solutions, and sugar has been added to limes to increase the action on the hides.

The following is the analysis of a lime used in a Leeds tannery, which was made by Mr G. W. Flower, B.Sc., in the Leather Industries Laboratory at Leeds University :[1]—

	Per cent.
SiO_2 and insoluble matter	17·70
Fe_2O_3	6·42
CaO	49·86
$CaCO_3$	14·21
$CaSO_4$	3·01
$CaCl_2$	0·33
MgO	2·09
Organic matter	0·80
Moisture by difference	5·58
	100·00

The sample only contained 31·02 per cent. of available lime, the remainder being probably combined with the silica. It also

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[1] *Journ. Soc. Chem. Ind.*, 1901, p. 224.

contained an appreciable quantity of iron oxide, which might lodge mechanically in the pores of the skin and become dissolved in later processes, darkening the colour of the leather. The lime was also under-burnt, judging from the amount of carbonate it contained.

For comparison with this, the analysis of a good specimen of carboniferous-limestone lime from Buxton may be given :—

	Per cent.
CaO	91·95
MgO	1·30
CO_2 and moisture	6·75
	100·00

Determination of "Available" Lime.—The practical value of lime for the tanner is easily determined by drawing a sample by breaking off small pieces from a number of lumps of the bulk, coarsely pulverising them in a mortar, and then rapidly grinding a portion as fine as possible, and transferring it at once to a stoppered bottle for weighing. A portion of this, not exceeding 1 grm., is shaken into a stoppered liter flask, which is filled up roughly to the mark with hot and well-boiled distilled water, and allowed to stand for some hours with occasional shaking. When cold it is filled exactly to the mark with cold distilled water, well shaken again and allowed to settle, or rapidly filtered, and 25 or 50 c.c. of the clear liquid withdrawn with a pipette and titrated with N/10 hydrochloric or sulphuric acid and phenolphthalein. Each cubic centimetre of N/10 acid equals ·0028 grm. CaO. If it be desired to determine separately the alkalies which may be present, standard N/10 oxalic acid may be substituted for hydrochloric, and after exact neutralisation a portion of the filtered solution may be acidified, and titrated with standard permanganate for soluble oxalates, but it is extremely rare that alkalies are present in such quantity as to justify this trouble. The process is unfortunately not applicable to used lime-liquors, as they contain organic matter which would also reduce the permanganate.

It is generally a very mistaken economy to make use of an inferior lime for tanning purposes, as any saving in cost is discounted by the larger quantity required, the more frequent cleaning of the pits, and the danger of stains and of burns from imperfect slaking.

The action of lime on the hide has already been spoken of to some extent. It is throughout a solvent one. The hardened cells of the epidermis swell up and soften, the mucous or growing layer and the hair-sheaths are loosened and dissolved, so that, on scraping with a blunt knife, both come away more or less completely with the hair (constituting " scud " or " scurf," Ger. *Gneist* or *Grund*). The hair itself is very slightly altered, except at its soft and growing root-bulb, but the true skin is vigorously acted on. The fibres swell and absorb water, so that the hides become plump and swollen, and, at the same time, the " cement-substance " of the fibres is dissolved, and they become split up into finer fibrils: the fibrils themselves become first swollen and transparent, and finally corroded, and even dissolved. A similar swelling of the fibres is produced by both alkalies and acids, and is due to weak combinations formed with the fibre-substance, which have greater swelling power than the unaltered hide.[1] This swelling is useful to the tanner, since it renders the hide easier to " flesh " (*i.e.* to free from the adhering flesh) on account of the greater firmness which it gives to the true skin. It also assists the tanning, by splitting up the fibre into its individual fibrils, and so exposing a greater surface to the action of the liquors. This is advantageous in dressing leather which is afterwards tanned in sweet liquors, and which must have the cement-substance of the fibres dissolved and removed for the sake of flexibility; and, in the case of sole leather, it is necessary for sake of weight and firmness that the hide be plumped at some stage of the process; but it is probable that this effect is produced with less loss of substance and solidity by suitable acidity of the tanning-liquors. Another advantage of lime is that it acts on the fat of the hide, converting it more or less completely into an insoluble soap,[2] and so hindering its injurious effects on the after-tanning process and on the finished leather. If strong acids, whether mineral or organic, are used later on, this lime-soap is decomposed, and the grease is again set free. In sweated or very low-limed hides this grease is a formidable evil, causing darkening or grease spots on the finished leather.

The customary method of liming is simply to lay the hides horizontally one at a time in milk of lime in large pits, taking care that each hide is completely immersed before the next is put into the pit, so as to ensure a sufficiency of liquor between them. Once a day at least the hides should be drawn out (" hauled "), the pit well plunged up to distribute the undissolved lime through the liquor, and the hides then drawn in again (" set "), care being taken that they are fully spread

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[1] *Cp.* Chapter X.

[2] This has been questioned, but I have satisfied myself it is correct.

out. Neglect of this to save labour is very unwise. How much lime is required is doubtful, but owing to its limited solubility, an excess, if well slaked, is rather wasteful than injurious. Great differences exist in the quantity of the lime used, the time given, and the method of working, not only for various classes of leather, but for the same kinds in different yards. Lime, as we have seen, is only soluble to the extent of about 1·25 grm. per liter (as 1 cubic foot of water weighs about 1000 oz.), say $1\frac{1}{4}$ oz. per cubic foot, or, in an ordinary lime-pit, not more than $\frac{1}{4}$ lb. per hide. Only the lime in solution acts on the hide, but it is necessary to provide a surplus of solid lime which dissolves as that in the liquor is consumed or absorbed by the hide ; and this is especially the case where, as is generally customary, the hides are laid flat in pits, so that no circulation of liquor is possible. Where hides are suspended in lime-water, which is constantly circulated and kept up to its full strength by agitation with solid lime, they unhair more quickly than when laid in milk of lime, and the method seems to be gradually superseding the older one, especially in dealing with more soluble depilatories. Various patents have been taken for methods of liming by suspending in liquors, but the idea is now public property, and is largely used on the Continent. It is necessary that the lime which settles to the bottom of the pit should be agitated and kept in suspension, which may be effected either by moving the hides on a frame as in "suspenders" (p. 356), or by agitators acting on the principle of pumps, and raising the liquor and sludge from the bottom. Such agitators have been patented in Germany, but had been in use much earlier in the Author's tanyard. An agitator on the principle of the screw-propeller of a steamship, placed near the bottom of the pit, and protected by a lattice, has been much employed on the Continent (fig. 30).

In England, suspension methods, though known for many years and in use in a few tanneries, received but little attention before the war ; but recently the saving of time, hide-substance, and labour which can be effected by suitable mechanical suspension and agitating appliances have led to their adoption in many large yards, often as more or less secret or patented processes, though it would be difficult to find a mechanical device which has not been used in times past. Such methods have the disadvantage of increased cost of plant, and the use of more pit space than is required by hides lying flat, though the latter is largely cancelled by the shortened time of the process and diminished quantity of lime required. The constantly increasing use of soluble depilatories, such as sodium sulphide, have also increased their relative advantage. They are frequently com-

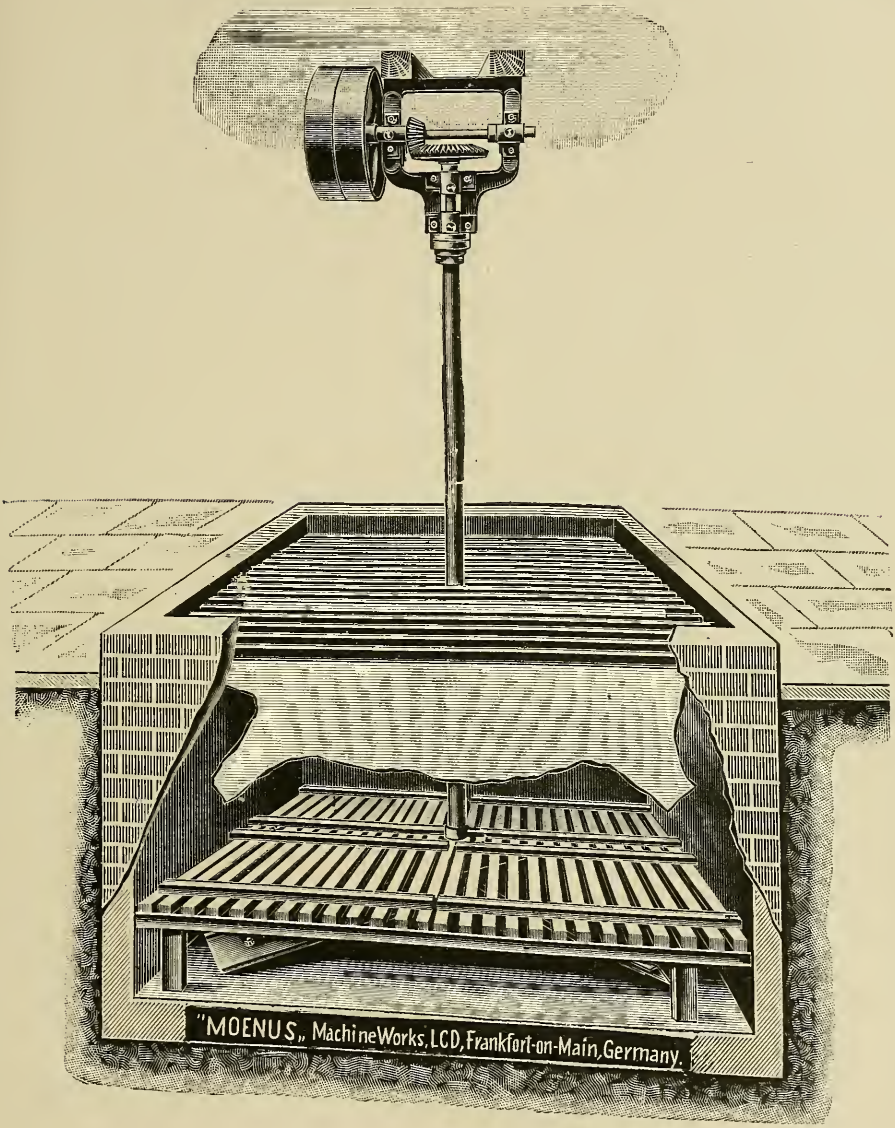

Fig. 30.—Suspension Lime-pit.

bined with means of mechanically handling the hides and removing them from pit to pit.[1]

Skins are frequently limed in paddles, or stirred up by blowing air into the pit. The latter method is neither effective nor economical in power for loose skins, but very convenient for suspended hides.

As has been noted, the solubility of lime, and consequently the strength of the lime-liquor, is diminished by rise of temperature, but its solvent action on hide-substance is much increased. As a consequence, the loosening of the hair proceeds much more rapidly in warm limes, but the hides do not plump well, and become loose, hollow, and inclined to "pipe" in the grain, and to "weigh out" badly, and for sole leather the method is therefore in every way disastrous. In the few cases among the lighter leathers, where a decided softening and loosening of the texture of the skin is required, it is possible that useful advantage may be taken of this effect ; but it would be exceedingly difficult to regulate the temperature of an ordinary lime-pit with accuracy, and better results could probably be obtained with suspenders in which the liquor could be constantly circulated. When limes are very cold, in spite of the greater strength of solution, the action is very much checked, and where goods are frozen into pits in severe weather, there is but little danger of over-liming, although the usual time may be much exceeded. It is generally best to work limes at about the ordinary summer temperature, and this is better done in winter by warming the lime-yard than by any direct heating of the limes. If lime which has cooled after slaking is used, the water with which limes are made may safely be warmed in midwinter to a temperature not exceeding 20° C.

The quantity of lime used by different tanners, and for different sorts of hides and skins, is very variable, not only according to the effect which it is desired to produce, and the way in which it is used, but from the arbitrary fancy of the user, since its limited solubility renders an excess comparatively innocuous. For sole leather, the amount recommended varies from under 1 per cent. to 10 or 12 per cent. on the green weight of the hide ; but probably 2 to 3 per cent. is all that can be really utilised, the remainder being wasted. In order, however, to utilise the whole of the lime, very frequent handling or agitation is required to ensure its uniform distribution. It must also be borne in mind that the strength of commercial limes varies from above 80 down to 30 per cent. of available calcium oxide.

Von Schroeder has found that a strength of 6 grms. of calcium

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[1] See Eng. Pats. 117581 and 124992.

oxide (CaO) per liter was sufficient, but, in practice, much more is generally added. It is also noteworthy that a perfectly fresh milk of lime is much less rapid in action than one which has been used. This is partially due to the fact that some bacterial action takes place in an old lime and that ammonia is formed which assists unhairing, in addition to the effect of the lime itself, and partially because the lime in old liquors remains in suspension for a much longer time, and is thus more evenly distributed.

A method of liming, sometimes known as the " Buffalo method," has been largely adopted for sole leather in America, and is now used in many Continental yards. It consists in a very short liming and the subsequent use of warm water. The limes are also often sharpened by the addition of a little sodium sulphide or of some other sulphide. Thus, in one large yard in the States, the hides for sole leather (salted " packers ") are limed for ten hours only with 2 lb. lime and 2½ oz. of sulphide of sodium per side, and after lying overnight in water of a temperature of 35° to 45° C. are easily unhaired. A Continental firm lime two days in weak fresh limes with a little tank-waste, and then treat with water at 32° C. for six to eight hours, when the hides are unhaired and returned to the warm water for two hours before scudding. All sorts of combinations between liming and hot-water treatment can be employed. The longer and stronger the liming, the lower temperature or shorter time in the water will suffice. The method is much to be recommended for firm sole leather, but it does not saponify grease or swell the fibres thoroughly, and usually sulphuric acid is used for the latter purpose in a later stage. The hide goes into the liquors practically free of lime, and the loss of hide-substance is much less than in the ordinary method of liming.

A point of probably much greater importance than the quantity of lime used is the length of time during which a lime is worked without change of liquor. An old lime becomes charged with ammonia and other products of the action of lime upon the skin, such as tyrosin, leucin (aminocaproic acid), and some caproic acid, the disagreeable goaty odour of which is very obvious on acidifying an old lime-liquor with sulphuric acid, by which considerable quantities of partially altered keratins are at the same time precipitated (*cp.* p. 134). A test supposed to indicate dissolved hide-substance in old limes has been employed in some yards, in which the liquor is slightly acidified with acetic acid, and an equal volume of saturated salt solution is added, when, on standing, a precipitate rises to the surface, the volume of which is supposed to indicate the dissolved hide-substance. (Cp. *L.C.P.B.*, p. 41.) It has been recently shown in the Procter International Research Laboratory that actual dissolved hide-substance is not precipitated under these conditions, and that the precipitate formed is entirely derived from the albuminoids (keratins) of the hair and epidermis, which it is the definite object of liming to dissolve.[1]

Lime has considerable antiseptic power, and a new lime is practically sterile, but very old limes, especially in hot weather, often contain large numbers of active bacteria, which may be seen in the microscope under a good $\frac{1}{6}$-inch objective. Their presence is always an indication that putrefaction is going forward, and if their number be very excessive, the leather out of such limes will generally prove loose, hollow, and dull-grained, and in extreme cases hides may be totally destroyed. Spherical concretions of calcium carbonate may also be seen under the microscope, resembling on a smaller scale those found in Permian limestone, and caused perhaps in both cases by crystallisation from a liquid containing much organic matter. It is hardly probable that in many tanneries the ammonia would pay for recovery from the lime-liquors, though it could be easily done by steaming the old limes in suitable vessels, and condensing the ammoniacal vapours in dilute sulphuric acid. Its quantity rarely exceeds 0·1 per cent. of NH_3. For methods of estimation of ammonia see *L.I.L.B.*, p. 30, and *L.C.P.B.*, p. 39.

Up to a certain point it is found that old limes unhair much more readily, and have a greater softening effect than new ones, which is often advantageous for dressing goods; though for sole leather, where weight and firmness are of primary importance, the use of stale limes must be kept within the narrowest limits. In the finer leathers also, such as kid and moroccos and coloured calf, where a sound and glossy grain is desired, the effects mentioned are generally better obtained in other ways, such as by the use of sulphides. On East India kips and other dried hides, which are difficult to soften, and which have great power of resistance to the action of lime, old limes are distinctly useful, but, even there, there are limits which should not be passed, and the tendency of modern practice is against their use.

Probably no lime ought to be allowed to go for more than three months at the outside limit without a change of liquor, and the system of allowing all the limes in a yard to run for twelve months, and then cleaning them all together, is almost the worst which can be planned. A very much better way is to

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[1] Thompson and Atkin, *J.S.L.T.C.*, 1920, p. 15.

clean the limes in regular rotation, using, if desired, a portion of the old liquor in making the new lime, so as to avoid a too sudden transition. The old liquor is valuable, if at all, for the ammonia and organic matter which it contains, as the amount of lime in solution is not worth considering. The ammonia considerably increases the solvent and unhairing power, while swelling the hide less than an equivalent amount of lime. In some cases it may be desirable to add ammonia artificially for this purpose. In this case it will be cheaper and more convenient to add it in the form of ammonium sulphate than as liquid ammonia. If it be desired to retain ammonia, the lime should be kept covered. Very old limes containing excess of ammonia and lime sometimes in hot weather cause a transparent swelling of the goods, with destruction of the fibrous texture.[1] This condition is not uncommon in sheep-skins which have been over-limed in fellmongering, or in order to make them sufficiently firm for splitting, and is known as "greenstiffness." Such skins come down with difficulty or not at all in the puers, and never make satisfactory leather. The writer has observed a similar phenomenon in very weak and old limes strengthened with sulphides, in which hide was left experimentally for several weeks. This effect is not fully understood, and deserves further investigation. The principal effect of the dissolved animal matter is to enable bacteria to thrive in it, which they will not do in a fresh lime, but putrid limes also contain liquefying ferments produced by the bacteria present (p. 19), which dissolve hide. Eitner published researches on the amount of hide-substance dissolved by limes, in which he shows that the loss of substance in liming sufficiently to unhair is materially greater in old limes than in fresh ones, although during the first two days of liming the new limes are decidedly the most active. As he remarks, this justifies the wisdom of the method, now largely adopted, of working limes in shifts, and beginning the operation in old limes and completing it in fresh ones. (See also p. 180.) He also proves that the loss in limes sharpened with sulphides is less than in those made with lime alone, and that they deteriorate more slowly. His methods of analysis are now somewhat antiquated, and do not differentiate between real loss of hide-substance and mere solution of epidermal matter, so that it does not seem worth while to reprint in detail, for which the reader must be referred to the original papers,[2] but he shows the very considerable loss which may occur in plumping limes after the hair has been removed.

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[1] *Gerber*, 1884, pp. 150, 184.

[2] *Ibid.*, 1895, pp. 157–9, 169–72.

The parts taken by the purely chemical activity of the lime, and by the action of bacteria and bacterial ferments in the unhairing process, must still be regarded as uncertain. The late Professor von Schroeder[1] carried out a series of experiments on liming and sweating which were characterised by his usual care and thoroughness, and which tend to prove that the chemical action is far more important than the bacterial. He had fresh hides well washed in a tannery immediately after slaughter, and fleshed. The butts were then cut into pieces of about 10 cm. (4 inches) square, and salted in brine repeatedly changed, and finally preserved for use in glass jars in saturated salt solution. He found that when washed free from salt, and placed in a moist chamber at a temperature of 16° C., the hair was sufficiently loosened by bacterial action in four to five days. Pieces placed in the moist chamber without previous removal of the salt only showed signs of sweating after about ten weeks' exposure. Liming experiments were made with similar pieces of salted hide, both after three days' washing to free them from salt, and unwashed, and in both cases the pieces unhaired freely in three to four days. These experiments were varied by using 6, 18, and 30 grms. of lime per litre of water in which about 200 grms. of hide were placed, but neither in the washed nor unwashed portions was there any material difference in the time required to loosen the hair. Addition of 1 vol. of used lime-liquor to 3 vols. of water in making up the limes was equally without perceptible influence, and careful bacteriological examination of hide and liquors showed that the former was almost sterilised by the intense salting, and that the lime-liquors were practically free from bacteria.

Von Schroeder's conclusion that no gain arises from the use of excessive quantities of lime, so long as the solution is kept saturated, is fully justified both by experience and scientific reasoning, but his results with regard to the effect of old liquors and bacteria contradict the conclusions both of practical tanners and of other scientific experimenters.

The different effects of old and new limes are too well known to practical tanners to be discounted by laboratory experiments, even if they were not confirmed not only by Eitner's results, but by a considerable amount of work done in the Author's laboratory and elsewhere; while the necessity of bacterial action is at least rendered probable by the fact that soda solutions which are completely sterile to bacteria, fail to unhair hides which have not previously undergone some putrefaction (see p. 183). In some

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[1] *Gerberei-Chemie*, Berlin, 1898, p. 646.

experiments undertaken at the suggestion of the Author it was found that a perfectly fresh and sterilised calf-skin which was not unhaired after ten days' liming in sterilised lime-liquor unhaired rapidly on the addition of a bacterial culture to the lime. It is extremely difficult to exclude bacteria, and even where perfectly fresh skins treated with chloroform or carbon disulphide were employed, bacteria were always to be recognised when the skin was ready for unhairing. Von Schroeder's work was, however, so painstaking and reliable, that these divergent results must be explained as other than experimental errors. With regard to old liquors, it is known that ammonia is a powerful aid to the unhairing process, and it is not certain to what extent the liquors he used were charged with it. It is also certain that old limes containing much organic matter support bacterial life freely, while 25 per cent. of a possibly not very old liquor would probably be sterilised by the addition of lime and 75 per cent. water. In order to test the matter fairly under exact tannery conditions, the lime should have been made up entirely with old lime-liquor well charged with ammonia and organic matters instead of with water. It is also probable that the hides had undergone a sufficient amount of bacterial change in the tannery before they came into Von Schroeder's salt solutions, and it is not at all unlikely that the salt solution itself exercised some specific effect on the unhairing. It is also possible that his bacterial cultures were made on gelatin media unsuitable for the growth of alkaline bacteria, and therefore gave blank results. Under these circumstances it is scarcely possible to arrive at any very definite conclusions, and it is obvious that further experiments on these points are extremely desirable.

Sodium and Potassium Hydrates.—From the earliest antiquity, wood-ashes, consisting mainly of potassium carbonate, have been used for unhairing, either alone or in conjunction with lime, and indeed the German name of the process (*Aeschern*) is derived from the fact. In more recent times, caustic soda, either ready formed or causticised on the spot by the addition of lime, has often been recommended as a substitute for lime. Its action is very similar to lime, but, from its greater solubility, is far more powerful, and probably this has hitherto formed one of the greatest obstacles to its use, since a solution of the strength of lime-water is almost immediately exhausted, while a much stronger one is too violent in its action on the hides. Some experiments made in the Author's laboratory appear to show that caustic soda, in solutions of the same strength as lime-water, dissolve considerably less hide-substance than the latter, but it is more antiseptic than lime, and does not unhair readily without the aid of bacterial action (*cp.* p. 183). It also swells more violently, and it is difficult to keep the grain smooth and unwrinkled, and, from its rapid action and the necessary dilution of the solution used, should only be employed in suspension-limes, or other appliances for rapid circulation of liquors.

Wilson points out [1] that the compounds of monovalent bases, such as soda, potash, and ammonia, are likely to be more ionisable and more soluble than those of divalent bases such as lime and baryta, and therefore to produce greater swelling and more solution of hide-substance, and this view is in accordance with known facts. J. Loeb has recently shown (*loc. cit.*) that the swelling power of acids and bases is inversely as the valency of the anions or kations respectively. For example, in solutions of equal hydroxyl-ion concentration, caustic soda exerts twice the swelling power of lime, since Na' is a monovalent, and Ca'' a divalent kation. Similarly hydrochloric acid has twice the effect of sulphuric acid in solutions of equal hydrion concentration. This work no doubt applies directly to hide and other proteins. Ammonia, it is true, swells less than lime because of its "weakness" as a base, which renders the actual concentration of hydroxyl-ions in an ammonia solution much less than in one of lime of equivalent concentration, but, notwithstanding this, it dissolves more hide-substance.

Caustic soda has the great advantage that from its solubility, and that of its carbonates in water, it is much more easily and completely removed by washing after neutralisation than is the case with lime. It has been successfully applied in some instances to soften skins of which the texture is naturally too compact for moroccos and the softer leathers, and is usefully employed in softening dried goods (p. 162). Where caustic soda is required merely to "sharpen" limes, it is best added in the form of sodium carbonate (soda-ash or crystals), which are causticised by the lime in the pits. One quarter or one-half per cent. on the weight of hides added in this way decidedly increases the plumping power of the lime. Some natural waters in Yorkshire contain sufficient sodium carbonate to produce this effect. It may be noted that in the use of sodium sulphide in conjunction with lime caustic soda is one of the products of its decomposition, and is one great cause of the difference of effect of this

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[1] "Theories of Leather Chemistry," *J.A.L.C.A.*, 1917, p. 112. See also, on this and many other important points, particularly sharpening of limes, E. Stiasny, *Gerber*, 1906, translated in *J.S.L.T.C.*, 1919, 4, p. 129.

material for sharpening limes as compared with red arsenic (*cp.* p. 189).

An indirect method of liming was patented by Messrs Payne and Pullman of Godalming,[1] which is of both scientific and practical interest. From the difficult solubility of lime, and the consequently weak solutions which must be employed, the ordinary process of liming is a slow one. Caustic soda, however, can be used in much stronger solutions without producing injury to the hide, or larger solution of hide-substance, as, from its great diffusibility, it penetrates very rapidly. Used alone, however, the hide becomes too much swollen for most purposes, and for certain classes of leather at least (*e.g.* buff and chamois leather) the presence of a portion of lime in the hide appears to be necessary for successful work. If a hide which has been swollen with caustic soda be afterwards treated with a solution of calcium chloride, double decomposition takes place, and caustic lime is formed actually in the interior of the fibre of the hide, while the sodium unites with the chlorine to form common salt. Both solutions may be used in any convenient way, and by the employment of drums the whole liming process may be accomplished in five or six hours. It was found, however, that perfectly fresh hides treated in this way could not be unhaired, and the explanation appears to be that in the ordinary liming process the epidermis is made soluble by the joint action of bacterial ferments and of the alkaline solutions. If sodium sulphide be added to the caustic soda used for unhairing the goods will unhair without the use of putrefactive means, but the process is difficult to manage without destruction of the hair, and Messrs Pullman later recommended that all hides or skins for unhairing by their process should be soaked for forty-eight hours in winter and twenty-four hours in summer in a really putrid stale soak. This necessity constitutes for very many purposes a serious weakness in the method, as putrid soaking is always extremely dangerous to the grain of the hide, and especially so in hot weather. For certain purposes, however, advantage may be taken of the fact that the hide or skin can be fully limed by Pullmans' process and the fibres swollen so as to be prepared for tanning without any loosening of the hair, and on fresh skins which have been treated in this way the hair remains perfectly firm, while they possess a softness and fulness which could not be attained without liming.

Messrs Pullman later recommended that the treatment with their solutions should take place in pits, in preference to drums or

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[1] Eng. Pat. 2873, 1898. E. M. Payne, J. & E. Pullman.

paddles, and that the caustic soda should not exceed a strength of 1 lb. in 10 gallons (1 per cent.). The hides or calf-skins remain in this for about forty-eight hours, during which they are once drawn and returned, by which time, if the putrid soaking has been properly done, the hair should be fully loosened. The hides are then drained for two hours, and passed into another pit containing a solution of calcium chloride, which should be slightly stronger than the caustic soda, say, of about 1½ lb. per 10 gallons. The goods remain in this for about forty-eight hours, during which they are drawn once, and are then well washed in soft water (free from temporary hardness), in which they may be kept for some time without injury. As the caustic soda and the calcium chloride solutions are quite sterile to ordinary putrefactive bacteria, both can be used for an almost unlimited time, and they are conveniently kept up to strength by the addition of strong stock-solutions. These may be made of a sp. gr. of 1·4 (80° Tw.), which gives a strength of about 5½ lb. of caustic soda and 5¾ lb. of calcium chloride per gallon.

In addition to the advantage of considerable saving of time, the effects can be much more easily regulated than in ordinary liming, and the amount of soda (and subsequently of lime) absorbed by the hide can be exactly determined by titration of the liquors. Grease is better removed than by ordinary liming, as soda-soaps are soluble in water, but if this result is to be obtained, the soap must be worked out before passing into the calcium chloride solution, which would otherwise convert it into an insoluble lime-soap. A great gain in many districts is that the process yields practically no effluents and no lime-slab, both of which are frequently very difficult to dispose of. The serious disadvantages of the stale soaking, however, have already been mentioned, and the method has not come much into use.

In place of applying the caustic soda first and the calcium chloride subsequently, hides may be first treated with calcium chloride solution and then with caustic soda, or the caustic soda may be applied to the flesh side of the hide by painting.

Alkaline carbonates are much milder in their action on hide than the corresponding hydrates, as they owe their effect to the small quantity of hydrate formed in their solutions by hydrolysis. As this is an equilibrium-reaction, and the hydrate is only reproduced as it is consumed, the effect is automatically self-regulating, like that of the limited solubility of lime. The unhairing action is somewhat slow and the swelling moderate, and they deserve more attention, but the best conditions for their use have not been sufficiently studied. In presence of lime they become causticised, and act like an addition of NaOH.

Sodium carbonate occurs in commerce in three forms: "soda ash," a more or less pure dry sodium carbonate; "soda crystals," or washing soda, $Na_2CO_3 . 10Aq$, containing 62·95 per cent. of water of crystallisation, and efflorescing in the air; and Gaskell and Deacon's "crystal soda," $Na_2CO_3 . 1Aq$, containing only 14·5 per cent. of water of crystallisation.

Sulphides.—The practice of using realgar, or red sulphide of arsenic (Ger. *Rusma*), as an addition to limes for fine leathers is one of considerable antiquity. It has the property of loosening the hair and epidermis structures with less solution of cement-substance than lime alone, and hence produces a leather of fuller and closer texture. It will, however, be convenient to defer the consideration of this agent till after that of some of the more modern and simpler substitutes, such as the sulphides of sodium and calcium. Sulphides of the alkalies and alkaline earths, if used in strong solution, say 5 per cent. or upwards, have the effect of very rapidly reducing the harder keratin-structures, such as hair and wool, to a pulp, attacking first the interior cells, so that each hair crumples up like a string of sausages, and in a few hours, or even, with very strong solution, in a few minutes, the whole mass becomes so completely disintegrated than it can be swept off the hide with a broom, or washed off in a tumbler. At the same time, the action on the substance of the hide, and especially on the cementing substance, is very slight, though the grain is swollen and temporarily rendered somewhat tender. On the other hand, when used in weak solutions, say $\frac{1}{4}$ per cent. and under, in conjunction with lime, the hair is but little injured, while the hair-roots and dirt are rapidly loosened, and results are obtained very similar to those with red arsenic.

Sodium sulphide ($Na_2S,9OH_2$).[1]—For the methods of valuation and determination of sodium sulphide, see *L.I.L.B.*, p. 28, and *L.C.P.B.*, p. 32.

It is very soluble in water, of which it combines with 1 mol., forming equal amounts of NaSH and NaOH.

Hides suspended in solutions of sulphide of sodium of 2 to 3 per cent. strength unhair rapidly.

For the commoner classes of sole leather, hair is frequently removed by painting on the hair side with a 15° to 28° Tw. (30

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[1] In the Laboratory Book the water of crystallisation is given as 10 Aq. Later researches show that pure crystals of the commercial sulphide only contain 9 Aq, or 67·5 per cent. of water.

to 40 per cent.) solution of (crystallised) sulphide of sodium thickened with lime, applied with a fibre-brush, and folding the hide in cushions in a damp place, or packing in a tub. The hair is reduced to paste in a few hours. The same effect is produced by drawing the hides through a similar solution without lime, of which sufficient is retained by the hair to destroy it. The workmen must be provided with indiarubber gloves to prevent the caustic effect of the solution on the skin and nails. Skins and lighter hides are conveniently unhaired by painting the mixture on the flesh side, when it will loosen the hair or wool in a few hours without destroying it.

For dressing leathers and the finer sorts of sole sodium sulphide is best employed as an addition to ordinary limes to the extent of $\frac{1}{4}$ to $\frac{1}{2}$ per cent. on the weight of the hides or skins, when the hair is loosened more rapidly than with lime alone, and with less loss of hide-substance.

Mixed with water to the extent of 2 to 3 lb. per gallon, and thickened with lime to a soupy consistence, it is much used for unwoolling sheep-skins. The wet skin is laid flesh up and painted with the mixture, care being taken that none of it touches the wool, which it would destroy. The skins are doubled down the back, and laid on loose boards so as to allow of drainage, the back of each skin being placed on the flank of the preceding, like the slates on a roof, and after lying overnight the wool is readily pulled, and the pelts receive a further liming to loosen the wool on the edges and complete the process.

It has been suggested by the Author that calf and other skins, which when chromed often prove loose on the flanks, might profitably be painted on the thicker parts on the flesh, possibly with a weaker solution than that just given, and after lying a short time, might be limed in the ordinary way to an extent only sufficient to loosen the hair on the thinner parts, so leaving them in a firmer condition.

For some classes of skins the powerful swelling effect of the sodium hydrate formed by reaction with water, and the further quantity by reaction of the sodium sulphydrate with the lime,[1] is objectionable, as causing too much swelling, and the use of arsenic sulphide, which does not produce sodium hydrate, is preferred. The difficulty can, however, to a large extent be

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[1] Professor von Schroeder expresses the opinion that lime and sodium sulphydrate do not react in this way, but, according to modern views, it is obviously an equilibrium-reaction, depending on the concentrations of the ionised portions of both, and at least some proportion must exist in solution, if not in a solid form.

overcome by adding an equivalent of calcium chloride, which reacts with the sodium hydrate, forming common salt and calcium hydrate. It is often said that sodium sulphide does not swell, and this is true when used for painting in strong solution on account of the repressive action of the concentrated solution, but if the goods are placed in water great swelling takes place, so much so that if allowed to soak too long they may become too swollen for convenient fleshing ; and there is no need for the subsequent swelling with sulphuric acid which is sometimes given, though neutralisation with this or some other acid is desirable, since, though all the products of the reaction are quite soluble, the compound of alkalies with hide is only very slowly decomposed by water alone. During the neutralisation a considerable amount of hydrogen sulphide is evolved.

Good samples of sulphide of sodium consist of pale brown, almost colourless crystals, containing 28 to 32 per cent. of dry sodium sulphide, which readily deliquesce on exposure to air. Fused sodium sulphide can now be obtained which contains nearly twice as much actual sulphide as the crystalline form. The dark green colour possessed by many samples of sodium sulphide is due to the presence of iron sulphide. If carefully used no serious harm can accrue from its presence. If allowed to stand a short time in solution the iron sulphide will settle out.

Calcium sulphydrate, $Ca(SH)_2$, sometimes called Böttger's *Grünkalk,* is a powerful depilatory, which has even less destructive action on the hide-fibre than sulphide of sodium, and would no doubt be largely used but for its unstable character. It is probably the principal active product produced by the use of sulphide of arsenic in conjunction with lime, though possibly a sulpharsenite may also be formed. It may be produced by passing hydrogen sulphide (SH_2) into milk of lime, or by the reaction of sodium sulphide on lime solutions. It may be obtained crystallised, and is soluble in water, but is decomposed on boiling, by the carbonic acid of the air, and by oxidation. The sulphide, CaS, is insoluble in water, but by the action of steam under pressure it is said to be converted into a mixture of equivalent parts of hydrate and sulphydrate. It may also be dissolved in a solution of hydrogen sulphide, forming a solution of sulphydrate. In this way it might be produced on a large scale from the " tank-waste " of the Leblanc soda process.

Gas-lime is principally active on account of the calcium sulphide which it contains, but is very variable in its strength, as both sulphydrate and sulphide are decomposed by the carbon dioxide always present in the gas, forming carbonates. Lime has nearly gone out of use for purifying gas, its place being now taken by iron oxide, but formerly gas-lime was a good deal used for unwooling the small lamb-skins used for the commoner sort of glove-kid, usually by painting a cream of it on the flesh side, but sometimes by immersing in a strong solution, which of course destroyed the wool. Its place is now taken by a solution of sodium sulphide of 15° to 18° Tw. (approximately 30 to 35 per cent. crystals), thickened with lime to a soupy consistence, the use of which is much to be recommended for unwooling sheepskins, by painting on the flesh.

The tank-waste from the Leblanc process, consisting principally of calcium sulphide, is, when fresh, quite insoluble, and has no depilatory powers ; but when exposed to air and moisture decompositions take place, resulting in the formation of sulphydrates and polysulphides, which form a solution which has been the subject of several patents for unhairing.[1] Polysulphides alone have probably no unhairing effect, but in conjunction with lime, sulphydrates are formed which rapidly loosen the hair. This fact was the basis of an ingenious and effective unhairing process used very many years ago by Mr John Muir of Beith, who, after liming for twenty-four hours in the usual way, submitted the hides to a pretty strong solution of weathered tank-waste for twenty-four hours, and finally to water for twenty-four hours, to remove the surplus lime and sulphides. The sulphydrates formed in the hide attacked the hair-roots with little injury to the hair itself, and the hides contained so little lime that they could be tanned for dressing without bating, and made about 10 per cent. more weight than those treated in the ordinary way. Some trouble was occasioned by stains caused by impurities in the tank-waste.

A somewhat similar unhairing mixture to that obtained from tank-waste, which is now seldom to be got since the introduction of the ammonia-soda process, was patented by Professor Lufkin,[2] who mixed equal parts of sulphur and soda-ash with a little water till combined, and then added 8 to 10 parts of lime, slaked and still hot. Schultz[3] states that such a mixture containing 10 lb. of sulphur will unhair fifty hides in the same way, and in about the same time as an ordinary lime, the pelt being little plumped and easily reduced without bating by a few minutes' wheeling in warm water. By boiling lime and sulphur with water a yellow solution is obtained which can be used in the

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[1] Squire, Eng. Pat. 756, 1855; Claus, Eng. Pat. 1906, 1855.

[2] Eng. Pat. 2053, 1860.

[3] *Leather Manufacture*, p. 35.

same way as that from the tank-waste. A further quantity of water can be boiled on the same materials, more lime and sulphur being added as required. Polysulphides appear to have a marked effect in preventing or reducing alkaline plumping, and apparently could be used in some cases with advantage as bates. On acidification they give off SH_2 and precipitate sulphur, so that if used for neutralising one-bath chrome leather they deposit sulphur on and between the fibres, and imitate that of the two-bath process, where sulphur is deposited by the decomposition of the thiosulphate. Sodium or potassium polysulphide can also be used for reducing in the two-bath process in place of thiosulphate. Sodium polysulphide is produced by boiling sodium hydrate, carbonate, or sulphide with excess of sulphur. It is a clear yellow solution, with a smell of hydrogen sulphide.[1]

Barium sulphydrate has been put on the market experimentally as an unhairing agent in the form of a strong solution containing yellow polysulphides, and which deposits crystals of sulphydrate in cold weather. It is more stable than calcium sulphydrate, but, on the whole, does not seem to present any great advantage over sodium sulphide, though it is quite effective as a depilitant.

Realgar or red sulphide of arsenic, As_2S_2, is made by fusing arsenious acid and sulphur, and is of somewhat indefinite composition. Mixed with lime it produces calcium sulphydrate, and possibly hyposulpharsenite. To produce a rapid and complete reaction it must be mixed with hot lime, and the hotter the mixture is made the more powerful is its unhairing action. Milder forms may be made by mixing cold, or with the aid of hot water only. It is used with great advantage in conjunction with lime in varying proportions for unhairing lamb- and kid-skins for glove-kid and other fine leathers, to which it gives the necessary stretch and softness and cleanness of grain, without the loosening of texture and loss of hide-substance which would be caused by an equivalent amount of ordinary liming. For glove-kid about 0·1 to 0·3 per cent. of realgar and 5 per cent. of lime is used, reckoned on the green weight of the skin. The mixture is added to the ordinary limes, according to the judgment of the tanner and the character of the skins.

For painting the flesh side of calf- and lamb-skins one part of realgar is mixed with ten parts of hot lime, made into a paste with water. Calf will unhair in eight or ten hours.

Orpiment (*auripigmentum*), As_2S_3, is the yellow precipitate produced in arsenical solutions by sulphuretted hydrogen, and is a by-product of the de-arsenification of sulphuric acid made from

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[1] See J. E. Pickles, *J.S.C.I.*, 1916, p. 456.

arsenical pyrites. It is consequently generally cheaper than realgar, and experiments in the laboratory of the Leeds Leather Department showed it to be more powerful as a depilatory, as is to be expected from its larger proportion of sulphur, but tanners for some reason, or very probably from prejudice, have generally refused to use it.[1]

An unhairing solution has been sold under the name of "Inoffensive" which contained a large quantity of arsenic sulphide apparently dissolved in caustic soda, although Moret's original patent claimed the use of wool-sweat potash only!

W. R. Earp[2] has suggested the use of compounds of sulphur and arsenic (thioarsenates, thioarsenites, etc.) in 5 per cent. alkaline solution. He prefers to add the compounds to the ordinary lime-liquors, or to manufacture them *in situ* by adding the proper quantities of arsenious or arsenic acid mixed with one-third of its weight of sulphur to a solution of an alkaline sulphide in lime-liquor. The pelt is not bated or drenched in the ordinary way, but, after unhairing, is passed directly into the tanning liquor, to which sulphurous acid has been previously added.

There is more danger of injury to the hide from the very prolonged action of weak solutions of sulphides, which tend ultimately to destroy the structure and reduce the fibre to a gelatinous condition, than there is from too concentrated solutions. No danger need, however, be apprehended in the course of any ordinary liming. Arsenical limes are not suited for tainted skins, and they should not be made so strong as to destroy the hair or wool.

All these arsenical compounds are very poisonous, and should go out of use for depilation, as they do not appear to be necessary. Alkaline solutions of arsenious acid are, however, useful in preventing insect-damage to dry hides, though they have little or no antiseptic effect, either for that purpose or in limes (see p. 42).

Dr Röhm, the inventor of "oropon" (see p. 220), has recently patented the use of the tryptic enzyme for unhairing as well as for puering. There is no reason that it should not do this quite effectively, as it digests epidermis matter without attacking the fibre of the hide, but it has not been sufficiently tried yet to enable us to pronounce on its commercial value.[3]

For the analysis of both old and new lime-liquors see *L.I.L.B.*,

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[1] See, on the action of arsenic sulphides, E. Stiasny, *loc. cit.*

[2] Eng. Pat. 2052, Feb. 12, 1886.

[3] *D.R.P.*, 268, 873. See also Hollander, *J.A.L.C.A.*, 1920, p. 477.

pp. 27–34, and *L.C.P.B.*, pp. 31–41. It must be admitted, however, that the present control-methods leave much to be desired in the determination of dissolved hide-substance and the distinction between this and the dissolved epidermis, but researches are in progress in the Leather Industries Department and the Procter Research Laboratory which promise a great improvement in this respect.[1]

Whichever method of loosening the hair be adopted, the actual removal must be effected by mechanical means, and is still very usually accomplished by placing the hide on a sloping beam with a convex surface, and then scraping it with a blunt two-handled knife (fig. 31), the workman pushing the hair downward and away from himself. The beam may be either of cast iron or of wood usually covered with zinc to increase its wearing capacity. The hides after being removed from the lime-pits are allowed to drain for half an hour or so before the hair is removed, and immediately this operation has been completed they should be placed in soft water. It is of great importance that the limed hides should not be exposed to the air longer than is absolutely necessary for the removal of the hair, as the carbonic acid present in the atmo-

FIG. 31.—Unhairing.

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[1] See four papers on Limeyard Control in *J.S.L.T.C.*, 1920, also Appendix.

sphere quickly carbonates any lime contained in the surface of the skin, forming chalk, and leading to uneven tanning at a later stage.

When hide has been insufficiently limed it is often easy to remove the longer hair but excessively difficult to get rid of the short under-growth of the young hairs, which even in properly limed skins can sometimes only be removed by shaving them with a sharp handknife. This difficulty is caused partly by the small resistance which the short hairs offer to the unhairing-knife, and partly by their being more deeply rooted in the skin than the older hairs (see p. 55).

Various machines have been devised to accomplish the removal of the hair, but owing to the rapidity with which it may be worked off by hand, and the fact that the work is not difficult, they have hardly as yet come into general use. Hand-work has the further advantage that in those portions of skin where the hair is tighter than usual it may be removed by greater pressure of the knife or by hand-shaving, whereas after goods have been unhaired by machine they must generally be examined, and any patches of hair removed by hand on the beam. The edges often require to be gone over by hand.

Several machines with spiral knives have been introduced for the purpose, but the great difficulty was the rigidity of the bed or beam on which the hide was supported, which often led to damage to the grain through any lump of flesh left on the hide. In this respect a great improvement has been made by the use of pneumatic rolls, on the principle of the motor-car tyre, into which air is continuously forced by a pump attached to the machine, the surplus escaping by a relief valve loaded to the pressure to which it is desired to inflate the roll (see fig. 37).

Another successful device is the Leidgen unhairing machine,[1] figs. 32, 33, in which the hide is supported on an apron of stretched canvas, while the spiral knife-roll not only rotates, but sweeps an arc down the hide, which is held in position during the traverse of the knife by an automatic clamp.

Occasionally goods are unhaired by fulling in the "stocks"; but the saving in labour is more than counteracted by the loss of weight caused by submitting the hide, while its gelatin is in a partially dissolved condition, to such rough usage.

The use of the wash-wheel (see pp. 158, 165) for the same purpose is much more satisfactory, and may be profitably employed for common goods when the hair has been destroyed by painting with a sulphide mixture.

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[1] E. H. Munkwitz, Milwaukee.

If a strong sulphide solution has been used, it may even be swept off with a stiff cane broom.

After unhairing the greatest care must be taken to avoid exposing the hide to the air, which always contains carbonic acid, or still more to water containing " temporary hardness," or free CO_2, and it is best to return them immediately to a pit of water which has been softened with added lime liquor, or which has been only partially renewed after use for a previous pack, and let them remain there till required for " fleshing."

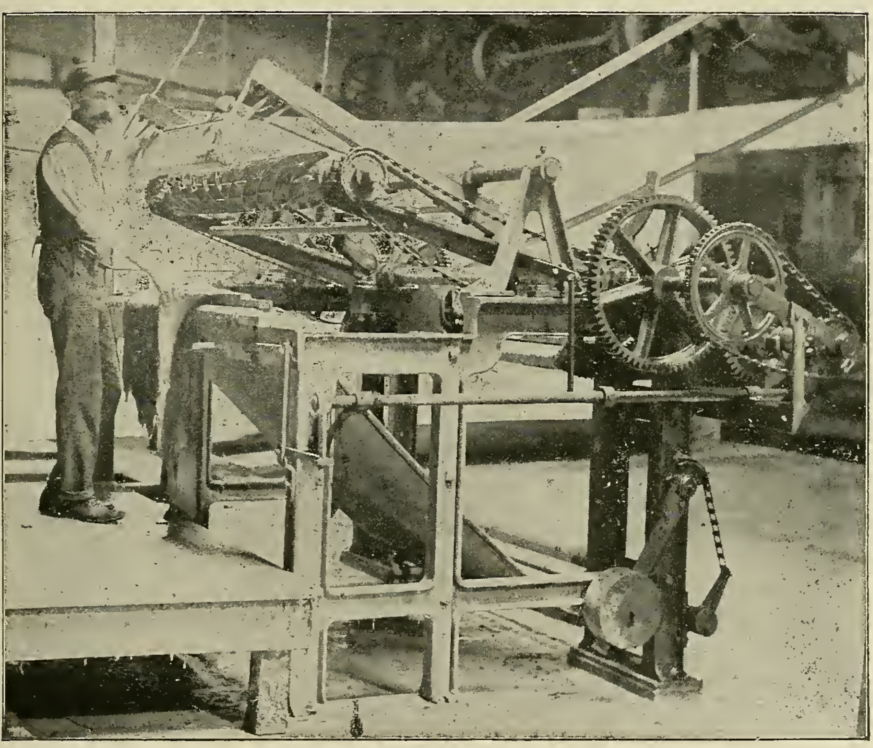

FIG. 32.—Leidgen Unhairing Machine.

After being unhaired, the hides are " fleshed " on the beam or by machine. This work, which consists in removing the loose subcutaneous tissue and any flesh and fat left on the inner side of the skin, should be carefully and thoroughly done ; but the closeness of the fleshing required is dependent on the purpose to which the hides or skins are to be applied.

It is necessary not only to remove those portions of fat which are easily visible, but also to force out that contained in the loose areolar tissue. The form of knife used in England in fleshing is shown in fig. 34. It differs from the one used on the beam for unhairing in being somewhat broader and heavier, and both its edges are sharp, so that where the flesh is too tight to remove by mere friction of the knife, it may be actually cut away by holding the knife almost flat on the beam and using the convex sharp edge. The knife is ground hollow on the surface next the hide. The strokes in cutting must not be too broad, or from the convexity of the beam the substance of the hide will be cut into in the middle, or "flesh" will be left at the edges of the stroke.

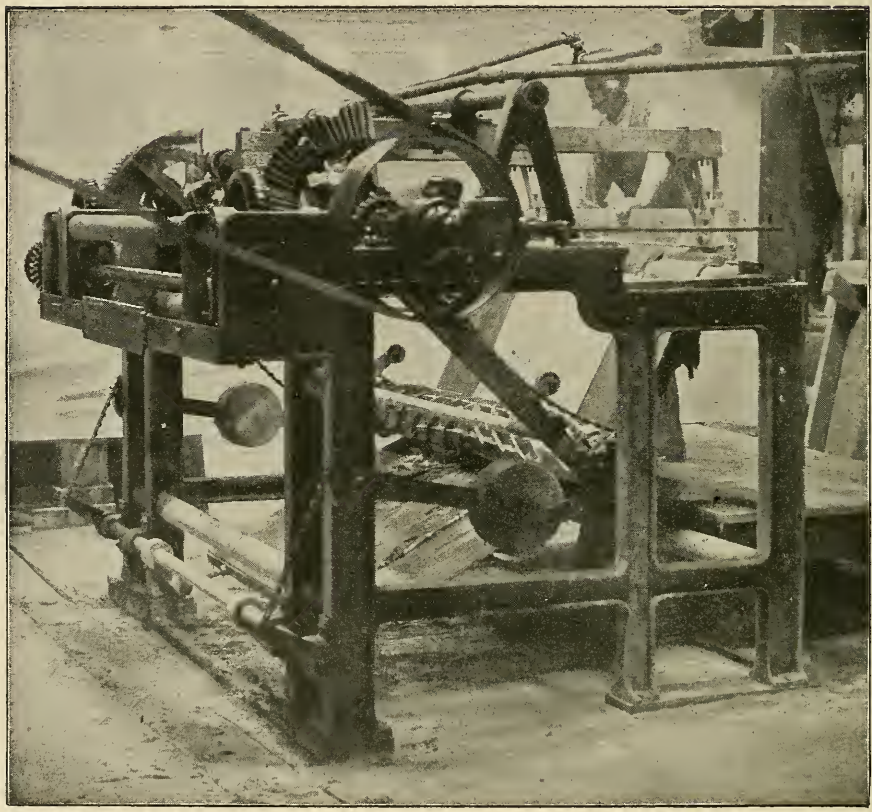

Fig. 33.—Leidgen Unhairing Machine.

This difficulty is avoided by the flexible knife commonly used in Germany, but in other ways its work is less rapid and effective.

Machines have long been used for fleshing and scudding light goods, such as lamb-, kid-, and goat-skins, and their use for fleshing dressing hides has now become very general in the United States, and is gradually gaining ground in England. The type of machine used for these heavier leathers varies considerably from that used for light skins, but the general principle is the same. In most cases the working tool of the machine is a cylinder with spiral blades, which are generally arranged right-handed on one half and left-handed on the other, so as not only to scrape the hide in the direction in which the cylinder works, but also to extend it sideways. Much of the efficiency of these machines depends on the exact adjustment of the pitch of the spiral, and in the Vaughn machine, which is probably most in practical use, the blades are so arranged as to form two intersecting spirals, one of steeper pitch than the other. The great difference in the machines for skins and for heavy work consists in the means adopted to support the skin and to carry it under the spiral blades.

FIG. 34.—Fleshing.

For heavy hides the Vaughn machine is most generally used, and may be taken as the type of the rest, as the Vaughn Company certainly originated the semi-cylindrical " beam," which forms a very important feature. Its construction will be seen from fig. 35.

It will be easily noticed that if a hide be thrown over the half-cylinder so that one half hangs outside it and the other half falls in its hollow, and it be then rotated, the hide is first caught firmly by a spring-clamp, which has been supported above the edge of the half-cylinder by blocks attached to the frame. As the edge rises it lifts this clamp off the blocks, and thus carries the hide under the spiral knife-cylinder. The blades of this spiral knife-cylinder are ground to a sharp rectangular edge, and partly scrape and partly cut the loose tissue of the flesh. When the half-cylinder has made a semi-revolution it returns to its original position, and the sizes of the driving pulleys are so arranged that the cylinder travels downwards more rapidly than it rises in order to economise time, though in both cases the hide is worked upon by the knife-spiral, which is rotated at a still higher speed. The hide is then turned on the beam-cylinder, and the other half is similarly fleshed. The beam-cylinder reverses automatically, or may be reversed by hand, and its nearness to the spiral knife is also under control. It is usually covered with a thick sheet of rubber.

It is obvious that machines of this type can be used not only for fleshing but for unhairing and scudding, by the substitution of suitable knife-cylinders.

The Vaughn machine is frequently used in America for fleshing hides after soaking but before they go into the limes, and much is to be said in favour of this method, as the removal of the flesh permits even and uniform action of the lime. It is, however, a distinct disadvantage to the method that the flesh appears rough-looking after tanning, and the method is most suitable in conjunction with the American system of splitting the tanned leather.

In the production of sole leather fleshing machines have not as yet come into very general use. This may be accounted for by the fact that if used before liming a rough flesh is produced, which is unsightly on sole leather, and which cannot well be afterwards improved, while something of the same objection attaches to fleshing after liming, with the added disadvantage that the hide is too much pressed, and is not easy to plump again so as to make a satisfactory sole leather.

What is really wanted is a machine which will really *cut* the flesh as the knife does. A machine which did this was invented by the late Mr E. Wilson, in which cutters something like the

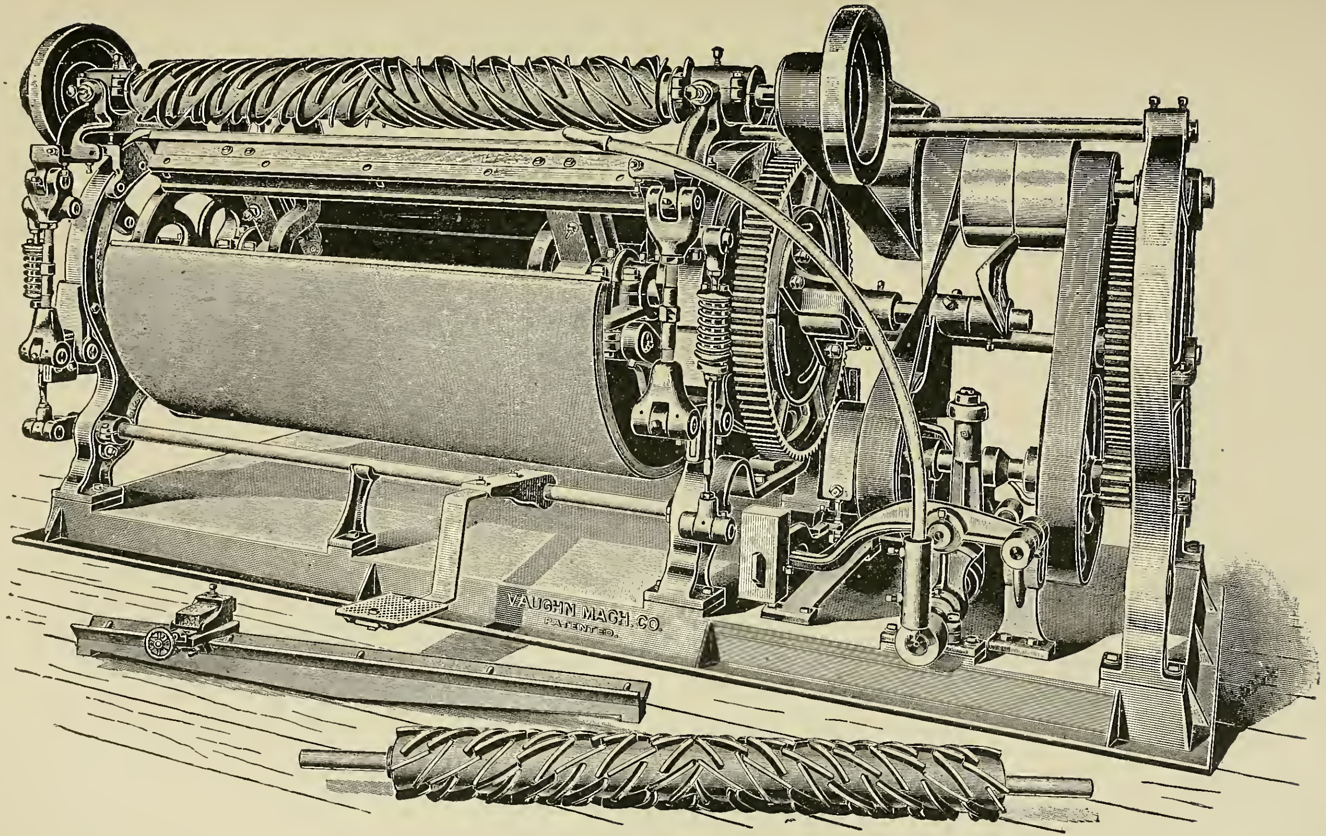

FIG. 35.—Vaughn Fleshing Machine, front view.

blades of skew-planes were attached to an endless band, which worked above a cylinder carrying the hide, and cut off the flesh almost like a splitting machine. It did excellent work, but was not much more rapid than hand fleshing. Dressing-hides are often fleshed in the States in the tanned condition by passing them through the band-knife splitter flesh side up, and with the machine so adjusted as to take a very thin skiving, the splitting proper being afterwards done in the ordinary way grain-side up. It is doubtful, but possible, that this might be done in the limed state with a machine with a grooved feed-roller, such as is used for splitting offal from the limes. The writer also suggested many years since that fleshing could be done by a machine like that used for shearing cloth, in which a spiral knife works against a fixed ledger-blade with a scissors-like action. The loose flesh would be drawn up by the rotating knife and cut off, while the firmer corium would pass under it, but, so far as he is aware, the idea has not been practically tested. In any case, at the present price of labour, machine-work is sure to come more into use.

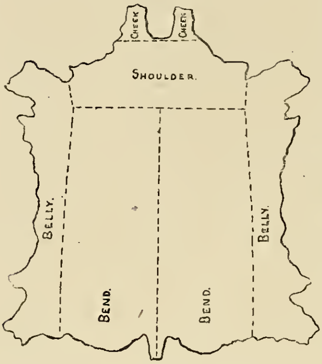

Fig. 36.—Diagram of Hide.

In America, both sole and dressing leathers are usually tanned in sides, the hide being cut down the centre of the back. In England, the hide is usually "rounded" for sole leather into "butts" or "bends" (half butts) and "offal," as shown in fig. 36. The rounding is done by hand with a sharp knife on a table, and in some of the best tanneries frames made of wood or metal are employed to mark the sizes required. The chief advantage of rounding before tanning is that the various parts of the hide can be differently tanned, and appropriated to the purposes for which they are most suitable. The offal is now frequently split either from the limes or after tannage and worked up for light leather, or in other cases is tanned with a cheaper and more rapid tannage than the butts.

Dressing leather is more frequently rounded after tanning, according to the purposes for which it may be required.

A considerable improvement has been made in recent times to fleshing, and some other leather-working machines, by substituting for a rigid, or simply rubber-covered roller supporting the hide under the spiral knife a pneumatic roller on the principle to the motor car tyre, which is kept inflated to any required pressure by a pump driven by the machine, and provided with a safety-valve allowing surplus air to escape if the pressure is exceeded. A machine of this type is shown in fig. 37.

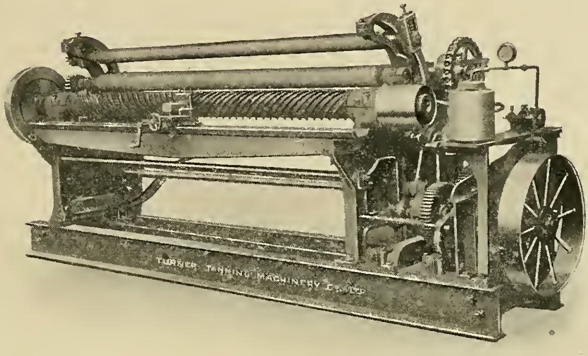

Fig. 37.

CHAPTER XIV

DELIMING, BATING, PUERING, AND DRENCHING[1]

ALTHOUGH lime is in many respects a most useful and satisfactory means of loosening hair, it is important that it should be completely removed, at least from the grain surface, when it has done its work, since its action on tannins is most injurious, and it is often harmful in tawing. For soft leathers it is also necessary that the skin should be brought from a swollen to a soft and flaccid condition.

All the processes mentioned under the heading of this chapter have the removal of lime for one of their objects, but, except in that of deliming with acids, they also fulfil other functions, such as bringing down the alkaline swelling, and removing certain constituents of the skin which are not required in the finished leather. All the older processes did this by means of bacterial fermentation, but it is now understood that it was by the agency of the enzymes or digestive ferments which the bacteria produced, and several modern bating preparations utilise the tryptic or pancreatic enzymes derived direct from animals.

The enzymes form a curious link between living and dead matter. Very small quantities are capable of breaking down large quantities of proteids into their simpler forms and, ultimately, into their amino-acids ; and they do this without themselves apparently suffering change. They are very selective in their action—the tryptic enzymes attack epidermis-matter and emulsify fats, but are unable to attack the unaltered hide-fibre itself, while pepsin digests the latter, but does not attack the epidermis nor fats. Most natural enzymes are mixtures, and it is quite possible that if we could completely separate them, we might find that each single enzyme could only digest one species of proteid ; and if we knew exactly what we wished to remove from skins, we might select the enzymes which would do it without touching anything else. The enzymes are also very particular as to the exact degree of acidity or alkalinity of the solutions in which they work, and each has an *optimum* hydrion concentra-

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[1] See also *The Puering, Bating, and Drenching of Skins*, by J. T. Wood. Spons, 1912.

tion; thus the pepsins will only act in faintly acid solutions, while the trypsins require alkaline media.

As regards the extreme "pulling down" effect of many of these fermentative processes no adequate explanation has yet been given, but it is a plausible, if as yet unproven, hypothesis that they automatically bring the alkalinity or acidity of the solution towards the isoelectric point (*cp.* p. 370) of collagen, which is the point of minimum swelling.[1] As the proteids are broken down towards amino-acids, their capacity for combining with acids or alkalies is vastly increased by the added number of free (terminal) amino-groups and carboxyls, and as the amino-acids themselves are *very* weak, either as bases or acids, they must ultimately bring down the hydrion concentration of the solution to a point very near neutrality. No decisive opinion can, however, be given till much more electrometric work with the hydrogen concentration cell has been done on these liquids.

The older methods may be described as follows:—

Bating consists in handling, or steeping, the goods in a weak, fermenting infusion of pigeon- or hen-dung for a time usually extending over some days, and is applied to the heavier classes of dressing leather, such as "common" and shaved hides, kips, and calf-skins.

Puering is a very similar process, applied to the finer and lighter skins, such as glove- and glacé-kids and moroccos, in which dog-dung is substituted for that of birds, and, as the mixture is used warm and the skins are thin, the process is generally complete in a few hours at most. Neither bating nor puering are very effective in removing lime, and seem to act principally by some direct effect of the bacterial products on the swelling of the pelt.

Drenching is occasionally used (*e.g.* on calf-kid) as a substitute for bating or puering, but more frequently follows the latter, and serves to cleanse and slightly plump the skins before tanning, and complete the removal of lime. The drench-liquor is an

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[1] Wood informs me that he has found the usual reaction of the bate is $P_H = 7{\cdot}0$, and the *optimum* concentration for the action of trypsin at 37° C. is P_H 9·7. The isoelectric point of collagen has been shown to be almost identical with that of gelatin, which is about $P_H = 4{\cdot}7$ or N/50,000, and thus slightly on the acid side of neutrality; but while the swelling curve rises rapidly on the acid side, it rises only very gradually up to about $P_H = 9$ on the alkaline. Bates and puers are usually faintly acid at the outset, and are only rendered alkaline by the lime removed from the skins, and the swelling is influenced by other ions beside H^+ and OH'. NaOH, which swells twice as much as its equivalent of $Ca(OH)_2$, is certainly removed in bating and puering.

infusion of bran made with hot water, and allowed to ferment under the influence of special bacteria, which are always present in vats used for the purpose, and which develop lactic and acetic acids.

It will be noted that all these methods are fermentative, and their effect is not simply the chemical one of removing the lime, but the bacterial action leads also to solution of the cementing substance of the hide-fibres, and produces a marked softening effect on the leather, together with considerable loss of hide-substance. In the manufacture of the softer leathers this effect is generally desired, and no process would be satisfactory which did not produce it ; but in other cases, such as harness- and strap-butts, firmer and heavier weighing leathers would be preferred if it were known how to make them. The putrefactive processes would be gladly relinquished if satisfactory substitutes could be found, not only on account of their offensive character, but because of their uncertainty and danger to the goods ; and even if lime only were removed, the necessary softness could often be obtained by appropriate liming and tanning.

It will be best, therefore, to deal first with the purely chemical methods which aim only at removal of lime before considering those involving bacterial action. Unfortunately, the chemical problem is not so simple as it might at first sight appear. The alkaline lime clings obstinately to the hide-fibre, and can only be removed partially by mere washing with water. On the other hand, the use of any considerable excess of strong acid is precluded, because of its powerful swelling effect on the pelt, in the tanning of which it would prove even more injurious than the lime, making dark-coloured and brittle, or tender, leather. This effect is not to be avoided by the use of even very dilute solutions of "strong" acids if used in excessive quantities, since the affinity of hide-fibre for them is so great that it will abstract practically all the acid from even a decinormal solution, leaving it quite neutral. What is required is an acid of extremely weak affinities, forming soluble lime salts, and obtainable at a low cost ; or, on the other hand, a salt of some weak base which could be displaced by lime, and which would not act injuriously on the pelt. With certain precautions, and in special cases, however, the stronger acids may be used successfully.

In the cases of sole and belting leather no softening is desired, and formerly tanners usually contented themselves with a very perfunctory washing in water, trusting to the acids present in the liquors to complete the removal of the lime. Even pure distilled water effects this removal very slowly and imperfectly, owing to the strong attraction of the lime for the fibre ; and if " temporary hard " water is used, the lime present in the hide combines with that present in the water and is precipitated as chalk in the surface of the hide. This may be prevented by previously adding a small quantity of lime or lime-liquor to the water before use to soften it (see p. 68) ; but unless this is very carefully done, the free lime present in the water prevents it from removing any from the hide. The safest way is not to add lime direct to the water, but to change the latter gradually, so as to allow the lime already present to soften the new portion of water.

Mere washing, however, is never thoroughly effective, and a much more efficient method is to suspend the butts in water to which small portions of diluted acid are successively added till the lime is nearly, but not quite, neutralised. If carefully used sulphuric acid may be employed, but, of course, any excess will spoil the colour or " buff " of the leather, and, unless the water is very soft, it always leaves calcium sulphate in the hides. Hydrochloric acid, though more costly, is free from this defect, but must not contain any considerable quantity of iron. For lighter leathers the writer has proposed the use of equivalent quantities of sulphuric acid and common salt, which J. T. Wood (*Bating, Puering, and Drenching*, p. 11) states is perfectly satisfactory.

For skins for puering, Wood only employs 4000 c.c. of hydrochloric acid of 18° Bè. (28·5° Tw.) for 250 kilo. of wet pelt, though this is only sufficient to dissolve about one-tenth of the lime present, since puering is an alkaline process. The process is best carried out in a paddle, beginning in cold water, and adding the much diluted acid very slowly, but towards the end warm water is run in to warm the skins before going to the puer. The acid should be added in at least three separate portions, say at intervals of ten, fifteen, and twenty minutes or longer. For details *cp.* Wood, *loc. cit.*, p. 8.

Acetic, formic, and lactic acids are safer than sulphuric, but are somewhat costly, and must not be used in appreciable excess. Crude pyroligneous acid may be used, and it has a considerable antiseptic effect owing to the phenols, etc., which it contains. Sulphurous acid[1] is perhaps the best, and its acid properties are so weak that slight excess does little harm, but the neutral calcium sulphite is insoluble, and to actually dissolve the lime the hydric sulphite must be formed, which can only occur in presence of excess of the acid. Unless such excess is used, the colour of the pelt in the early liquors is apt to be somewhat

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[1] Manufacture of sulphurous acid, see p. 24 ; testing, see *L.I.L.B.*, p. 37, and *L.C.P.B.*, p. 13.

greyish. Probably a very good method would be to suspend the butts in a deep pit, preferably provided with some means of agitation, in a solution of sulphurous or some other acid of about N/20 strength, sufficiently long to remove all lime from the surface and slightly to plump but not to penetrate to the centre of the hide, which should then be suspended in water until any excess of acid had been taken up by the unneutralised lime still present in the middle of the butt, which at the end of the operation should be rather alkaline than acid. The course of this, or any other deliming, operation can be followed by cutting the hide, and moistening the cut surface with alcoholic solution of phenolphthalein, which is turned red, or pink, by the least trace of *free* lime.

In using mineral acids it is of great importance that they should be perfectly free from iron, and that the vat employed should contain no iron which could become dissolved, since, if present in the bating liquid, it is sure to be fixed by the hide, especially if the quantity of acid used is insufficient to neutralise the whole of the lime.

Besides the direct use of mineral acid which has been described, sulphuric or, still better, oxalic acid may be very advantageously employed in precipitating lime from used bating liquids containing weak organic acids or other lime solvents, so as to restore their original activity. Not only is the bate economised by being used repeatedly, but some of the organic products dissolved from the hide have themselves considerable power of removing lime. Putrefaction should not be allowed to take place ; but many of the organic acids which have been proposed for bating belong to the aromatic series, and have considerable antiseptic power. Where organic acids are employed, the presence of their neutral lime-salts in the liquor, resulting from previous operations, will reduce the swelling action of the acid on the skin without diminishing its power of removing lime, but neutral salts of strong acids have little effect on the strong acids (*cp.* p. 100).

Ordinary sodium bisulphate has the disadvantage of leaving practically the whole of the lime, in the form of calcium sulphate, in the hide, and therefore is only suitable for sole leather, but it can be used for the purpose, and its action is more mild than that of sulphuric acid itself, but great care must be taken that no nitric acid is present, as is frequently the case in the crude product obtained in the manufacture of nitric acid from sodium nitrate, and known in commerce as " nitre-cake." The presence of a trace of sodium chloride would not be disadvantageous for dressing leather, but would tend to prevent plumpness in sole.

Paessler and Appelius [1] have shown that raw hide absorbs sulphuric acid from sodium bisulphate, leaving the neutral sulphate in solution.

Boric (boracic) acid, though used to a slight extent for a number of years past, has recently come much into favour as a deliming agent, for which purpose it is in many respects particularly suitable. Sole leather may be improved in colour by giving a short bath in 1½ to 2 per cent. boric acid solution to remove surface-lime. In this case the acid is best applied just before the hide enters the suspenders. Boric acid may also be suitably employed on hides which have been bated. It then acts as a drench and removes traces of lime still left in the hides, so that the liquors have a more even effect on them. Experience has shown that the skins should never be allowed to lie for any length of time in the boric acid solution in a motionless condition, as this tends to produce patches of partially delimed skin, which cause irregular colour. It is best to keep the skins in fairly constant motion in a paddle or by frequent handling. Boric acid has considerable influence in preventing drawn grain in the early liquors, but if it gets into the forward liquors it renders the leather loose and light (*cp.* p. 370, and *L.I.L.B.*, p. 37, and *L.C.P.B.*, p. 12).

Borax has also been suggested as a deliming agent, and as it is chemically an acid salt, it has naturally some deliming effect, but it cannot compare with boric acid in either price or efficiency.

Both boric acid and borax are antiseptics (see p. 26).

In the employment of either sulphuric, boric, or any other acid forming calcium salts of limited solubility, it must be borne in mind that if the solution is repeatedly re-strengthened it will become saturated with the lime-salt, and although the acid will still combine with the lime and render it neutral, it will no longer remove it from the hide. Under these conditions, sulphuric acid may cause the deposition of crystalline calcium sulphate in minute nodules between the fibres. Calcium borate may be similarly deposited, and has the further disadvantage of becoming decomposed by the tanning liquors, which form dark compounds with the lime. In using sulphuric or boric acid alone it is therefore best to renew the water each time. When it is used in conjunction with some other acid, forming very soluble lime-salts, this danger is not to be apprehended, while oxalic acid precipitates the lime almost completely from the solution.

It is to be borne in mind that in all cases of using acids, any carbonate of lime present on the pit sides or elsewhere will be

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[1] *Wissenschaftlich-Technische Beilage des Ledermarkt*, 1901, p. 107.

decomposed, and the carbonic acid will become dissolved in the liquor, and unless acid is used in sufficient quantity to remove the whole of the lime, may tend to fix the remainder as carbonate. In the case of dressing leather there is less danger of this, as warm water is generally used, in which little carbonic acid dissolves. It is probable that some of the coal-tar sulphonic acids which have been advertised for bating dressing leather might be advantageously employed for sole, and if the liquor were regenerated by the addition of sufficient sulphuric acid to neutralise the lime dissolved from the hide, might be used repeatedly, and would not then prove expensive ; while their sterilising power would be very advantageous to the proper swelling of the butts in the handlers, since nothing tends to check plumping so much as putrefactive action.

Turning from sole to dressing leather, mineral acids are very successfully employed for "pulling down," the goods being thrown into a paddle containing warm water of about 30° to 35° C., and the calculated quantity of sulphuric or hydrochloric acid, previously largely diluted with water, is then added in successive portions at intervals, and more gradually and slowly the thicker the hides. The acid must in no case be sufficient to neutralise quite the whole of the lime. Goods treated in this way can be further bated, puered, or drenched as required by the ordinary methods if they are not sufficiently soft. If too much acid has been used, and the skins show signs of swelling, they must be brought down by the addition of a little ammonia, or even soda, as if swollen with acid they will not bate with an enzyme-bate.

In many cases the addition of salt in small quantity to the acid liquor will tend to deplete the hides, and at the same time prevent any injurious action of the acid. Ammonium chloride may also be used with advantage (see p. 209). A solution containing about 15 per cent. of salt and 0·3 per cent. of sulphuric acid, with some molasses, has been a good deal used in the States as a deliming agent, and seems to answer well on some classes of goods, but the acid and salt are apt, ultimately, to find their way into the liquors and destroy tannin. The process is well suited for chrome leather, and may also be usefully applied in cases where goods have become "wind-blasted" or otherwise impregnated with carbonate of lime, since in presence of salt the acid can be used in sufficient excess to dissolve the carbonate. Vegetable acids may, of course, be used in conjunction with salt in the same way. The salt does not neutralise the acid, but simply controls the swelling of the skin, and if acid has been used in any material excess, the first part of the tanning must be done in salted liquors, or the acid neutralised with ammonia, sodium carbonate, or chalk previous to tanning, as, otherwise, the goods will plump up in the liquors, and be tender when tanned (*cp.* p. 237).

Lactic acid has recently come largely into use as a deliming agent. It is best known as the acid which gives a characteristic taste to sour milk, and is the chief product of the lactic ferment. It may be very successfully used for neutralising the lime left in the skins after the depilation, but, if used in excess, it tends to plump or swell the leather. When used for deliming, a solution of 2 lb. in 100 gallons is very suitable. It may, in many cases, be substituted for the bran-drench with advantage, and is much more rapid and less dangerous in hot weather, but the effect is not in all respects identical.[1]

When lactic acid is used for bating or drenching the operation should always be conducted in a paddle, and the liquid works more satisfactorily if it is at a temperature of 30° to 35° C. As regards cost, it will be found that in practice it is not appreciably more expensive than dung or bran. About an hour's paddling will generally suffice if the right quantity of acid has been used, but in some cases it is best to add the acid in several portions and take more time, and of course the thicker the hides the longer the time required.

The estimation of the amount of lactic acid in the commercial article may be carried out by diluting exactly 9 grm. with about ten times its volume of water, and then titrating it with normal caustic soda as described in *L.I.L.B.*, p. 16, for acetic acid, and *L.C.P.B.*, p. 12. As each cubic centimetre of normal alkali is equivalent to ·090 grm. of lactic acid, it will represent 1 per cent. of real lactic acid in the sample. If other acids are present, they are of course included. Commercial lactic acid is usually of about 50 per cent.

It is important that the lactic acid should be free from iron; a dilute solution should give no blue coloration on addition of either potassium ferrocyanide or ferricyanide. Acid perfectly free from iron is now easily obtained.

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[1] On the manufacture of lactic acid by fermentation, see Claflin, *Journ. Soc. Chem. Ind.*, 1897, p. 516. Campbell states that practically pure cultures of the lactic bacteria are obtained by continued culture in milk. These cultures employed as a ferment for drenches made with glucose have given good results in the Leeds University Experimental Tannery. The addition of a little used liquor will assist the fermentation, which should be kept slightly warm, say 30° to 40° C.

It has been shown in the Procter International Research Laboratory that the lactic anhydrides always present in commercial lactic acid are of equal value to the acid itself for deliming, and become converted into the acid on dilution. Their separate estimation is therefore useless.[1] In fact Dr G. Eberle proposed the use of such anhydrides for deliming purposes, for which they would be very suitable in cases where it was desirable to keep down the amount of free acid to a minimum. The anhydrides of acetic, propionic, butyric, and lactic acid, as well as the lactone of γ-oxybutyric acid and the lactide of lactic acid, are specified.[2]

Formic acid in 60 per cent. solution, formed synthetically by the combination of carbon monoxide with caustic soda and the subsequent decomposition of the sodium formate so produced, has been brought into commerce at a cheap rate, and forms a satisfactory substitute for acetic acid in the deliming of hides and many other technical operations. Formic is about ten times "stronger" than acetic acid. Wood (*loc. cit.*) says that a mixture of equal parts of formic and acetic acids acts better than either alone. It is said that the formate of lime formed has a "pulling down" action, and that less than the theoretical quantity is therefore sufficient.

Butyric acid, produced by the process of Dr Effront of Brussels, was on the market commercially before the war. It is a still "weaker" acid than acetic, and, as was to be expected, dissolves still less hide-substance, and if it can be produced sufficiently cheaply, should prove very valuable to the tanner.

The following table, calculated in 1911 on the then price of commercial acids, gives the cost of neutralising 1 lb. of lime (CaO) with each ; and though, of course, the present prices differ considerably, the relative cost probably remains much the same. The very greatly heavier cost of the weaker organic acids shows the importance of liberating them again after use by the addition of sulphuric acid. The cost per lb. of lime is calculated by the formula $\frac{\text{pence per cwt.} \times 100 \times \text{eq.}}{112 \times 28 \times \text{per cent. strength.}}$

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[1] Thompson and Suzuki, *J.S.L.T.C.*, 1918, p. 115.

[2] *Verfahren zum Beizen der Haüten*, *Ledertechnische Rundschau*, Nr. 24, 1910. *Coll.*, 9, 1910, p. 372.

COST OF ACIDS TO NEUTRALISE 1 LB. OF LIME.

Acid.	Equiv.	$K = 100\,k$.	Cost per cwt.		Strength. Per cent.	Cost in pence.
			s.	*d.*		
Hydrochloric	36·5	Very large	3	3	31·5	1·4
Sulphuric	49·0	Very large	4	0	95·0	0·8
Oxalic	63·0	0·1	30	4	99·0	7·4
Formic	46·0	0·0214	35	0	87·4	7·0
Lactic	90·0	0·0138	26	0	49·7	18·0
Acetic	60·0	0·0018	18	0	40·0	10·8
Butyric	88·0	0·00115	21	0	82·8	8·5
Boracic	62·0	0·00000001	27	0	99·0	6·5

k is the dissociation-constant of the acid, and indicates its chemical "strength." Note the excessive weakness of boracic acid, which will not even redden litmus (*cp.* p. 99).

Attention must here be drawn to a very important paper by Stiasny[1] on the applications of the law of mass action to deliming and neutralisation of chrome leather, processes similar in principle though apparently very different.

Instead of acids, many neutral salts may be used to neutralise lime, and in sole leather it is not generally disadvantageous to leave the lime in the hide, so long as it is in an insoluble and fixed condition, and combined with an acid which cannot be displaced by tannin. Thus phosphates or oxalates of sodium or ammonium will convert the lime into insoluble phosphate or oxalate, setting free sodium- or ammonium-hydrate which forms soluble tannates and other salts which are easily washed out of the hide. Zinc sulphate will form sulphate of lime and zinc oxide in the hide, and seems worth further experiment for sole leather, but must be free from iron. It has some tanning effect, and has been used in conjunction with vegetable tannins. Alum, or sulphate of alumina, would similarly form calcium sulphate and alumina, but the tanning effect of alumina salts is too great to admit of their general use for bating, though they are very suitable for chrome leather. Ammonium sulphate will form calcium sulphate with liberation of ammonia.

For dressing leather the use of ammonium chloride is still more advantageous, and it is a powerful bating material, converting the lime into calcium chloride with the evolution of ammonia, which is a very weak base, and has but little plumping power, and is easily washed out. Ammonium chloride has been

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[1] *J.A.L.C.A.*, 1912, p. 301.

very successfully used in calf-kid manufacture as a preparation for drenching instead of puering, which was formerly in vogue. As, however, only about $\frac{3}{4}$ oz. per dozen skins was employed, the cleansing must have mainly depended on the warm water with which it was used and the free ammonia evolved. Wood states [1] that ammonium chloride should not be used in greater concentration than 0·7 to 1·0 grm. per liter, or the skins become leathery and do not fall properly. It is always used in conjunction with pancreatic bates, in which it serves the double purpose of removing lime and of activating the trypsin ferment.

The use of ammonium chloride as a bate was patented by Zollickoffer in 1838.

A bating liquor which was proposed by the writer, and which has been used with some success on harness leather, is made up with $\frac{1}{4}$ lb. of good white ammonium chloride (sal ammoniac) and $\frac{1}{4}$ lb. of Boakes' "metabisulphite of soda" per hide, and for successive packs sufficient sulphuric acid is added to neutralise the ammonia formed, together with a small quantity of metabisulphite and ammonium chloride to restore that carried out by the hides. It is probable that this would also answer well for deliming sole leather, as it entirely removes lime without pulling down the hides much, and they would remain still plumper if ammonium sulphate were substituted for ammonium chloride, while the sulphuric acid might be safely increased till the liquor was but slightly alkaline when the bating was finished. About 2 to 4 oz. of good white oil of vitriol is required per hide, but the exact quantity will depend on the mode of liming and the amount of washing the hides receive before going into the bate, and can therefore be only ascertained by experience. As no free sulphuric acid can exist in the liquor so long as the quantity of metabisulphite is maintained, there is no practical danger of spoiling the leather if the acid be in slight excess. The quantities given may in most cases be advantageously diminished, since it is not always advisable in practice to remove the whole of the lime, which in small quantity renders tannage and penetration of the liquor much more rapid, either by acting as a mordant to the tannin, or by temporarily neutralising it and diminishing its astringent action on the hide-fibre.

Turning to dressing leather, we find that the use of cold water alone has been practically abandoned in this country, though the finest French calf is produced by repeated soakings in cold water with alternate workings over the beam, sometimes extending to nine or more. In this case, from the lengthened exposure

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[1] "*Puering, Bating, and Drenching,*" p. 47.

to waters which are only gradually renewed, it is probable that putrefactive action takes place, and that a sort of bating is effected by the decomposing products of the hide itself; in fact, in many French yards bran-drenches have been introduced to supplement the action of the water alone. Waters differ greatly in their power of removing lime from skin. Slightly acid and peaty waters, and those in general which contain much organic matter, are much more powerful in reducing than those which are purer (*cp.* p. 82).

Warm water has much more effect in removing lime than cold, since the heat lessens the risk of dissolved carbonic acid, and seems to have a direct depleting effect on the pelt. A good tumbling in warm soft water will remove a great deal of lime, and is an excellent preparation for bating, but heat must be used cautiously, and should never exceed 30° to 35° C.; some skins, such as seals, being very readily tendered by its action, while others, especially sheep-skins, will stand a comparatively high temperature.

The temperature which skins will stand without injury depends not only on the nature of the skin, but on its condition; skins in a neutral condition will stand considerably higher temperatures than those swollen with lime or other alkalies, or probably than if swollen with acid. The following table, due to E. Munro Payne, is an estimate of the highest temperatures which skins will stand without injury, but probably makes no claim to great exactness:—

Limed skins	27°–28° C.
Hide-substance . . .	40° C.
Alum leather . . .	50° C.
Tanned leather . . .	71° C.
Oil leather	84°–85° C.
Chrome leather . . .	106° C.
Aldehyde leather . .	222° C.?

The use of a solution of carbonic acid for removing lime has been patented by Nesbitt,[1] who takes advantage of the fact that calcium carbonate is soluble in excess of carbonic acid (p. 67). The gas, which he generates as for soda water, by the action of acids on chalk or limestone, is received in a gasholder, and forced by a compressing pump into the vessel containing the hides, which is preferably a rotating drum lined with copper, and capable of bearing a pressure of about three atmospheres. The invention excited considerable interest on its introduction, as the gas is,

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[1] Eng. Pats. 7744 and 12,681, 1886.

certainly, quite uninjurious to the hides, and it was claimed that it enabled the grease and dirt to be better removed than by the ordinary methods. Further experience has shown, however, that the removal of the lime is far from complete, since, for success, it is not only necessary to bring it into solution, but to wash it out with carbonic acid solution under pressure, as on exposure to the air solutions of lime in excess of carbonic acid rapidly deposit calcium carbonate. The only tannery in which to my knowledge the process has been extensively used is that of Messrs Mossop and Garland, of Capetown, who stated that it answered very well for harness leather when a pure lime made by calcining sea-shells was used for liming, but was not satisfactory with ordinary stone lime. It is difficult to account for this on chemical grounds. Gluestuff may be treated very satisfactorily by simply blowing carbon dioxide, or washed and cooled lime-kiln- or furnace-gases, into an open pit, in which the material is kept agitated. In this case, however, there is no need for the actual removal of the lime, so long as it is carbonated and its caustic character destroyed. Carbonic acid does not decompose lime-soap, and hence sets free no fatty acids, which, together with grease, are the main cause of the turbidity of glue, and the process therefore yields a more brilliant though darker coloured glue than does treatment with sulphurous acid.

Several acids of the aromatic series have been from time to time recommended as deliming agents, and generally possess the merit of acting at the same time as powerful antiseptics. In this connection it may be well to mention the solution of 1 per cent. of phenol and 2 per cent. of boric acid used by Dr Parker and the writer for preparing and preserving skins for colour tests (*L.I.L.B.*, p. 133, *L.C.P.B.*, p. 115). This answers very well as a bate even when much diluted, and may be rendered cheap enough for use in practice by the employment of a good commercial carbolic acid instead of pure phenol, and the use of sulphuric acid to remove lime from the solution renders it capable of repeated employment. The carbolic acid should not be too dark in colour, and should be carefully dissolved, or "carbolic" stains will result.

"Cresotinic acid," a mixture of impure acids obtained from cresols in the same way as salicylic acid is manufactured from pure phenol, was introduced as a bate and unhairing and deliming agent by J. Hauff, of Feuerbach.[1] He also claimed the use of hydrochloric acid to liberate the acid after it had been combined

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[1] Eng. Pats. 10,110 and 12,521. *Journ. Soc. Chem. Ind.*, 1889, pp. 124, 809; 1890, p. 85.

with lime in the deliming process. It is only soluble to the extent of about 1 in 800 of water, so that, even if used in excess, no dangerously strong solution is formed, but it has a tendency to swell slightly, and somewhat harden, the hides or skins, so that it is perhaps more suitable for sole than dressing leather. It has also powerful disinfectant properties. Hauff[1] afterwards patented the use of oxynaphthoic acid, the corresponding mixed naphthol-acids. Oxynaphthoic acid is only soluble in 20,000 to 30,000 times its weight in water.

A mixture of the α and β mono- and di-sulphonic acids of naphthalene has also been patented by Burns and Hull,[2] and later Hauff[3] patented a mixture of various impure sulphonic acids of cresols and hydrocarbons. All these patents are now expired. Cresol-sulphonic acids are the first stage in the manufacture of Stiasny's "syntans," and are afterwards condensed with formaldehyde.

All these coal-tar "bates" are to replace drenching rather than bating or puering, as their effect is mainly that of removing lime. From their antiseptic character they are very useful in stopping the effects of putrefaction and preventing ferments being carried into the tanning liquors, and skins may safely be kept at least for some days in weak solutions, but any necessary fermentative puering or bating should usually be done before and not after their use. If used before puering they would no doubt stop any direct bacterial action on the skin, if not in the puer liquor, but they probably would not prevent the action of the bacterial enzymes already formed, and their use might afford a means of using bacterial enzymes without the danger inseparable from actual bacterial puering or bating.

A writer in the "Gerber," 1875, p. 279, recommends the use of dilute solution of sulphide of sodium as a bating agent. Possibly it removes lime as sulphydrate, and the writer named seems to have obtained good results with glove lamb-skins, but experiments made at Leeds were not successful. Possibly what he really used was a polysulphide. Polysulphides, such as "liver of sulphur," or the yellow solution obtained by boiling dilute sodium sulphide or sodium hydrate solution with excess of sulphur, have great power of "bringing down" the pelt, and seem well worthy of experiment as bating agents.

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[1] Eng. Pat. 14,889, 1888. *Cp.* also *Journ. Soc. Chem. Ind.*, 1889, p. 954.

[2] Burns and Hull, Eng. Pat. 8096, 1891; *Journ. Soc. Chem. Ind.*, 1892, p. 48.

[3] J. Hauff, Eng. Pat. 22,546, 1894; *Journ. Soc. Chem. Ind.*, 1895, p. 170; Gerber, 1895, p. 133.

In India the pods of the babool (*Acacia arabica*) are much used as a bate, the infusion being allowed to ferment. In their dry state they contain about 12 per cent. of an easily changeable tannin, which does not precipitate lime-water, and which by fermentation is very probably converted into gallic acid. The use of gallic acid itself as a bate has been patented by Albert Hull,[1] and would undoubtedly accomplish the removal of the lime if used in sufficient quantity; but as he only uses a solution of 25 mgr. per litre (one part in 40,000), any effect must be mainly due to the washing with water. Gallic acid forms dark oxidation products with lime.

Of the fermentative methods of removing lime, "drenching" with fermenting bran-infusions is the simplest in theory, and has been very carefully investigated by Mr J. T. Wood.[2] It will, therefore, be convenient to consider this process first, although it is frequently employed as a means of cleansing and slightly plumping the skin after the lime has been removed by puering or bating. In calf-kid manufacture, however, it is used without previous puering, and in some other cases it is substituted for the use of dung bates. The most important of the active ferments are two species of bacteria, named by Wood *Bacterium furfuris* α and β, which are very similar in their form and action (see *L.I.L.B.*, p. 264), but produce a somewhat better fermentation together than separately. They are shown in figs. 38 and 39.

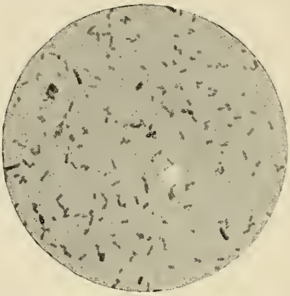

FIG. 38.—*Bacterium furfuris α.*

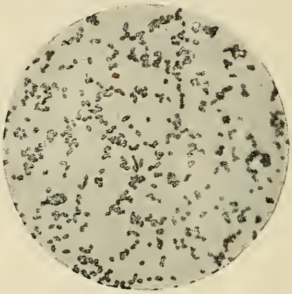

FIG. 39.—*Bacterium furfuris β.*

Neither species has any direct action on the hide-substance, but ferments the glucose produced by the action of the cerealin of the bran on the starch which is present. A considerable quantity

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[1] Eng. Pat. 14,595, 1889.

[2] *Journ. Soc. Chem. Ind.*, 1890, p. 27; 1893, p. 422; 1897, p. 510; *Brit. Assoc. Rep.*, 1893, p. 723. See also *The Puering, Bating, and Drenching of Skins*, by J. T. Wood. E. & F. N. Spon, Ltd., 1912.

of hydrogen, with carbon dioxide, nitrogen, and small quantities of hydrogen sulphide, are produced during the fermentation, together with lactic and acetic and traces of formic and butyric acids and amines. Active drenches contain 1 to 3 grm. of mixed acids per litre, to which they owe their action, a perfectly satisfactory drenching being produced by an artificial drench containing 0·5 grm. of glacial acetic acid and 1 grm. of lactic acid (sp. gr. 1·210) per litre, in which the skins were worked for one and a half to two hours, while twelve to sixteen hours would have been required in the ordinary drench. An experimental drench gave the following results on analysis :—

Formic acid	0·0306 grm. per litre.
Acetic acid	0·2402 ,,
Butyric acid	0·0134 ,,
Lactic acid	0·7907 ,,
Total	1·0749 ,,

It is probable that other organisms are capable of producing similar fermentations, and it is not certain that in all tanneries the same ferments are present. Mr A. N. Palmer stated that at the Cambrian Leather Works at Wrexham he was unable to detect lactic acid in the drenches, all the acids present being of the acetic series.

The drench-ferments investigated by Wood are incapable of attacking or injuring the hide, and, in his opinion, when the skin is attacked, it is generally due to putrefactive and gelatin-liquefying organisms introduced from the bates, or from the air in hot sultry weather. Drenching takes place most safely and satisfactorily at temperatures not exceeding 30° to 35° C., when the process is usually complete in twelve to twenty-four hours. In sultry weather a butyric (?) fermentation of an active character sometimes suddenly takes the place of the normal one (Ger. *Umschlagen*), the skins swell rapidly, become translucent (*gläsig*), and finally dissolve to a jelly. If tanned in the swollen condition, tender and useless leather results, and the injury, once begun, proceeds with alarming rapidity, skins being sometimes completely ruined in a few hours. Prompt action is therefore necessary, and the first step to take is to add salt, which checks the fermentation, and acts in the same way as in the pickling process, controlling the action of the acid, and producing a sort of tawing. Such skins will yield sound leather, though the grain is apt to be somewhat drawn. If the skins can be immediately got out of the drench, the acid may be neutralised by the cautious addition of ammonia, soda, or whitening to the water in which they are placed, preferably in a paddle, and if they are insufficiently drenched they may then be paddled in tepid water, though this is hardly likely to be needed, as the effect of the acid is to remove the lime very completely. The objection to the use of whitening, which otherwise is the safest and best material to employ for removing acid from pelt, is that it is apt to become mechanically fixed in the grain, and thus to produce bad colour with vegetable tans. For white or chrome leather it would do no harm. Precautions to prevent the recurrence of the injury are to keep the temperature of the drench low, and to free the bran from flour by washing in two or three cold waters before adding to it the hot water with which the actual drench-liquor is made, since the flour, or at least its starch, is the source from which the butyric acid, as well as the lactic, is formed. This trouble is rare in the comparatively cold climate of England, and indeed the writer has never seen a case, or had the opportunity of investigating one. It is hardly probable that it is really due to butyric acid, since it is now known that butyric acid is an extremely mild one, milder than acetic or lactic, though of course in very large quantity it could produce the effect. It may be due to the production of some other acid, or possibly of some bacterial peptic enzyme, which liquefies and digests the hide-fibre. In cold weather, where drenching is proceeding in a normal way, the flour is useful, since it is the natural nutriment of the drench-ferment; and, in England, flour is frequently added purposely to the bran to increase the activity of the drench. To retain the flour, the bran may be washed first with boiling water, which gelatinises the starch and makes it adhere to the bran, and, according to Eitner, removes a sticky fat-like matter from it, and fits it better to remove the fat of the skin. After soaking in hot water for two hours it is washed in several cold waters and infused at about 40° C. for use.[1] Many tanners use the bran without previous washing, but if much flour is present it rises to the top with the gas evolved by the fermentation, and forms a pasty mass on the skins, which interferes with even drenching.

The quantity of bran used in ordinary drenching is very variable, but about 4 parts per 1000 of water used and from 5 to 10 per cent. on the weight of pelt may be taken as an average quantity, more being frequently employed. The temperature may vary from 10° up to about 30° to 35° C., and the time inversely from days or weeks down to two or three hours, according to the temperature of the drench, the amount of ferment

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[1] Gerber, 1882, p. 246.

present, and the thickness and character of the skins. The skins are usually thrown into the freshly prepared drench, to which a few pailfuls of old drench-liquor is frequently added as a ferment. Fermentation soon sets in, and the gas evolved causes the skins to float to the surface ; this is called the " working " of the drench. Thin skins may be sufficiently drenched after once rising, while thick ones require to be put down two or three times. A certain sign of sufficient drenching is the appearance of small blisters on the grain, caused by the evolution of gas in the substance of the skin. When these are seen the drenching should be at once discontinued, as otherwise the blisters will increase in number and burst through the grain, causing minute holes or " pricks " (one of the many forms of the complaint called in German *Pikiren* or *Piquieren*). When a bubble of air is enclosed in a fold of the sufficiently drenched skin and pressed, it raises the grain without actually separating it from the substance of the skin. The properly drenched skin also falls easily in folds when held between the hands either lengthways or crossways, and if thin the skin tightly stretched over the hand shows grains of bran underneath it as little lumps, round which the skin clings to the hand. The drenched skin should not be transparent, but white and soft, and when pressed should retain the mark of the finger. Some experience is required to determine certainly the point of sufficient drenching, which, of course, varies with the character of the skins and the kind of leather which is to be produced ; and the feel of the skin to a practised hand is one of the most important criteria.

A writer in the "Gerber "[1] divides drenching for glove-lamb into three classes . " sweet," " alcoholic," and " sour." Sweet drenching is done in a bath of tepid bran-water, made by infusing in hot water and drawing the clear liquor off the bran, which settles to the bottom. The skins are only allowed to remain in two or three hours, or not long enough for fermentation to set in. The process is only suited for very thin or soft skins which will not stand any further loosening. The use of bran-water has the advantage of saving the labour of " branning," or removing adhering bran with the knife on the beam, but it is doubtful if unfermented bran has much actual effect. Bran-water can, however, be used for drenching by fermentation, and for small glove-lamb has largely superseded the older method. The mechanical action of the bran in cleansing the pelt is however often useful. In sour drenching the bran is allowed to steep and soften in cold water for many hours, and boiling water is then added till the

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[1] Gerber, 1888, p. 257.

temperature is raised to 75° C., and it is allowed to infuse with frequent stirring for some hours, and after cooling to 45° a considerable quantity of old drench-liquor is added as a ferment. If the drench is used warm (30° to 35°, or in cold weather, even 40° C.) the skins only remain in one to three hours, but if cold the drenching can be extended over a period of two to three days, the skins being frequently handled. This modification is suitable for glacé-kid and the harder sorts of skins, but glove-lamb are always treated by the warm and rapid process. What the writer in the "Gerber" describes as the "alcoholic" bran-drench is probably the method of fermentation investigated by Wood, in which inflammable gases, but no alcohol, are produced.

A normal drench plumps the goods slightly, but if it contains much of the putrid ferments carried in from the bate or puer the skins fall in it as they would do in a bate. To increase this effect, putrid soak-liquor is sometimes added to the drench, but with doubtful advantage.

In drench-liquors the total acidity may be determined by titration with lime-water or N/10 caustic soda, with phenolphthalein as indicator; and the volatile acids may be distilled off as described under the analysis of tanning liquors (*L.I.L.B.*, p. 126). For more complete methods of analysis the reader is referred to Wood and Willcox's paper on the "Nature of Bran Fermentation."[1]

Drenches are said to "work" somewhat better if made with water containing nitrates, and this is quite probable; but the necessary nitrogen can easily be supplied if required by the addition of a very small quantity of saltpetre.

Wood is of the opinion that the ferments found in bran do not originate in the drench itself, but come from the bated skins, as the drench-bacteria soon die out without finishing the fermentation, and constant renewing of the nutrient material is necessary (*cp.* p. 18).

Bating and *puering*, though differing practically in many ways, are identical in theory, and most of what follows applies to both of them. The action is much more complex than that of the drench, involving both chemical reactions and those of organised and unorganised ferments, and it is a matter of no little difficulty to say what proportion of the observed effect should be ascribed to each of these agencies.

Formerly, the principal effect was attributed to organic salts of ammonia and its homologues, and to amino-acids which com-

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[1] *Journ. Soc. Chem. Ind.*, 1893, p. 422. *Cp.* also *Puering, Bating, and Drenching of Skins*, p. 233.

bine with lime. Phosphoric acid is also present, and if any exists in the form of soluble salts, it will combine with lime, and render it insoluble and inactive. It is probable, however, that most if not all the phosphoric acid is already in the form of tricalcium phosphate, and therefore without effect.

It is now, however, recognised that the effects of these chemicals are of no importance as compared with the products of bacterial action, and the researches of Wood have cleared up much that was until recently quite inexplicable.[1]

Much effect was formerly ascribed to the digestive ferments, such as pepsin and trypsin, which are present in fresh dung. It is known that the animal organism secretes these in considerable excess of its requirements, but it is doubtful whether any exist undecomposed, even in fresh dung; though they are apparently more resistant to putrefaction and decomposition than would *a priori* have been expected of such complex organic compounds, and there is therefore a possibility of their existence in the dung, even as it comes to be used in the tannery. Both pepsin and trypsin are enzymes (see p. 15), and are possibly proteins. They are soluble in water but insoluble in alcohol, and hence are precipitated by the addition of the latter to their solution, but are not altered by it, and regain their activity on solution in water. Wood separated puer enzymes in this way fifteen years ago. They have been kept in a dry state, and are as active to-day as when first prepared. By heat they are coagulated and decomposed, and their activity permanently destroyed.

Pepsin is the active principle of the secretion of the glands of the stomach, and large quantities are prepared for medical use as an aid to digestion from the stomachs of pigs. Pepsin only acts in slightly acid solution, and though fresh bate liquor is slightly acid to litmus, it speedily becomes alkaline from the lime of the skins and the ammonia present, so that the action of pepsin in a bate can only be a very limited one. Wood[2] compared the action of a 1 per cent. solution of pepsin, acidified with 0·2 per cent. of hydrochloric acid, with that of a dogs'-dung puer liquor, both at the temperature of 40° C. At the end of one hour the skin in the pepsin-solution was considerably fallen, but that in the puer solution was almost dissolved. Since the solution here employed was much stronger than is likely to occur in practice, and the conditions much more favourable to its action, it may be assumed that the practical effect of traces of pepsin

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[1] *Journ. Soc. Chem. Ind.*, 1894, p. 218; 1895, p. 449; 1898, pp. 856, 1010; 1899, pp. 117, 990; 1912, p. 1105.

[2] *Ibid.*, 1894, p. 220. *Cp.* also *Puering, Bating, and Drenching.*

from the stomach in the bate may be neglected. The peptic enzymes of the larger intestine, which are more likely to be found in dung, are bacterial in their origin, and though 0·2 per cent. of HCl is the *optimum* for the pepsin of the stomach, it is too high for those of the intestine.

Trypsin or *pancreatin,*[1] if present, is more likely to have an effect, since it is active in neutral and in alkaline solutions. It is the product of the pancreas, and is largely concerned in intestinal digestion. Chemically it much resembles pepsin, but is more resistant to heat, retaining its power of digestion after heating to a temperature of 160° C. in a dry condition. Its warmed solution dissolves fibrin almost instantly and in large quantity, and peptonises gelatin so as to render it soluble in water. Wood found that a 1 per cent. solution of pancreatin acted far more rapidly than a solution of pepsin of equal strength. At 40° C. in neutral solution the skin fell rapidly, and the action continued even in the cold. In fifteen hours the liquid was swarming with minute bacteria. At the suggestion of the Author the experiment was therefore repeated, with the addition of 15 per cent. of chloroform, which prevented the development of bacteria while it did not stop the action of the pancreatin. The skin fell as before, but in neither case had it the peculiar touch of puered skin, nor were the characteristics of the leather produced from it the same. Wood found later that the unsatisfactory result of this experiment was due to the presence of excess of lime and the want of ammonia, which is necessary to activate the pure pancreatic ferment. In the body this is done by a special enzyme, enterokinase, which is secreted in the small intestine. The practical pancreatic bates, such as "pancreol" and "oropon," contain ammonium chloride. This addition was due to Dr Röhm, who patented oropon in this country, but the principle was covered in America by a previous patent of Wood's.

It is certain, however, that fresh bird-dung, and probably that of all animals, contains ferments capable of liquefying gelatin. An instance of this is found in the observation, common in glue manufacture, that if the dropping of a sparrow falls on a cooler full of solidified gelatin size, it will liquefy a track quite down to the bottom of the cooler. Trypsin, or at least the secretion of the pancreas, as well as the gall from the liver, have great power of wetting and emulsifying fats, and this has possibly something to do with the action of the bate in enabling the skins to be cleansed of fat.

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[1] *Loc. cit.* and *Beilstein,* iii. p. 1308, 2nd edition.

Bacterial fermentation and its products are, however, the main factor in the action of puers and bates, and on this subject we owe most of our knowledge to the work of J. T. Wood, since, though Popp and Becker have worked over much of the same ground, they have not nearly so freely published their results.

Wood showed that a fresh puer liquor, even when boiled for half an hour, and so freed from living organisms and albuminoid ferments, has still considerable action on a limed skin, though much less than the unboiled puer. He found that this action was principally due to amines and their compounds with organic acids, which removed lime, but did not remove the interfibrillary substance or give the proper feel of puered skin. A very similar result was obtained with aniline hydrochloride in 1 per cent. solution.

A considerable variety of bacteria from dung and other sources were cultivated in various media and their puering power tested, but though greater than that of the unorganised chemical compounds such as amine salts and organic acids, it was in no case equal to that of an ordinary puer, or sufficient for practical use. When, however, a small quantity of the amine salts obtained from the puer was added to a mixed bacterial culture the effect on the skin was almost as rapid and considerable as with an actual puer.

In order to determine whether the puering effect was due to the direct action of the bacteria or to their enzyme-products, the latter were separated from a filtered puer solution by adding it to a large volume of 98 per cent. alcohol, in which the enzymes are insoluble. When redissolved in water they had a decided puering effect, and a solution of 0·5 grm. of the mixed enzymes and 0·5 grm. of the mixed amine hydrochlorides in 100 c.c. of water at 35° C. brought down a piece of limed sheep-skin in thirty minutes exactly like a puer. The action is therefore dependent on the mutual action of the enzymes and amine salts, but as the separation of these would be too costly for practical use, and the puering seemed effectual when they were formed in contact with the skin by active bacteria, Wood adopted the method of preparing a suitable sterilised nutritive liquid, which was inoculated before use with a mixed culture of suitable bacteria. For laboratory purposes a suitable culture-medium was obtained by digesting 10 grm. of gelatin with 5 grm. of lactic acid (reckoned water-free) and 100 c.c. of water for three hours in a closed vessel on the water-bath. The resultant solution was neutralised with sodium carbonate and diluted to 1 litre with addition of a small quantity of potassium phosphate.

The bacteria of fresh dog-dung were not found to produce a satisfactory puering effect, but those from dung which had been fermented a month (as in practice) gave a result nearly equal to actual puer. A still better result was obtained by a mixed culture from the roots of wool loosened by sweating. The bacteria were principally of two species, of which neither separately was capable of satisfactory puering, but which together acted more rapidly than an actual puer. These bacteria do not liquefy gelatin.

During the course of his experiments Wood found that filtered puer solutions were less active than turbid ones, and that their activity was increased even by the addition of inert substances, such as kaolin.

Wood attributes the differences in action between dog-dung and bird-dung not only to different bacteria, but to the fact that in the latter case the urinary products, and especially uric acid, are contained in the dung.

From the results of these and similar researches, Wood in England and Popp and Becker in Germany succeeded in producing a practical artificial puer, which they manufactured in conjunction under the name of " Erodin," consisting of a solid nutrient medium and a liquid " pure culture " of the bacteria necessary to effect the required bating or puering.

The preparation was quite successful, and superseded dog-dung in many tanneries, though for sheep- and goat-skins it never quite took its place, but for calf it proved much safer and less liable to cause stains. Details of its use are omitted, as it has been almost entirely replaced in its turn by pancreatic preparations, which are still safer, and can be better modified to suit the leathers which are being produced.

The pancreatic bates were suggested by Wood's work on the pancreatic ferment, which has already been mentioned, but though he included its use in an American patent, he did not at the time pursue the idea, thinking that the use of pure cultures of bacteria offered better prospects of success. His idea was, however, taken up by Dr Röhm [1] in Germany, who produced the very satisfactory bate " oropon," and a similar preparation, with some improvement in detail, is now being produced under the name of " Pancreol."

The instructions for using " Pancreol " for calf- and sheep-skins intended for either vegetable or chrome tannage are as follows:—The limed skins are partially delimed either by thorough washing with soft water or by the use of weak organic acids. The skins are then warmed up and partly bated in a weak " Pancreol "

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[1] Ger. Pat. 200,519, 1908.

bath made by diluting half the liquor used for the last pack with hot water. The temperature should be 95° F., and the skins are paddled for fifteen minutes. The main bating liquor is prepared by diluting the remaining half of the old liquor with hot water so as to bring the temperature to 98° F. The required amount of "Pancreol" (about 9 to 12 oz. per 100 lb. of pelt) is then added and stirred in for five minutes. The goods are then introduced and paddled for twenty minutes. Afterwards the skins are paddled for a few minutes every quarter of an hour until they are sufficiently bated. This occupies one to four hours according to requirements. The amount of liquor used should not be more than 25 to 30 gallons per 100 lb. of pelt. After bating, the skins are carefully scudded, and washed in warm, clean water. Subsequent treatment is just the same as with skins bated with excrement bates. Users are warned not to dissolve "Pancreol" in *boiling* water. This is of course very injurious to the enzymes. The above instructions require modification for other classes of skins, etc., but there is no change in principle.

In addition to trypsin, the pancreas also secretes the enzyme steapsin, which has the effect of emulsifying and saponifying fats, but like trypsin is inert as secreted, and requires to be energised by ammonia or enterokinase. As these enzymes only act in alkaline solution, care must be taken, if the skins are delimed with acids before the bate, not to carry the action too far, but to leave some lime in the skin.

These pancreatic bates are being more and more widely used, sometimes with the addition of fat-emulsifying enzymes, and with varying quantities of ammonium chloride to remove lime, and are likely as their use is more fully understood to take the place of fermentation-bates and puers for all kinds of leather.

Considerable light has been thrown on the real object of puering, which obviously accomplishes more than the mere removal of lime and of the remains of the hair follicles and fat-glands, by the work of Rosenthal and Wilson in America,[1] Moeller in Germany,[2] and Seymour-Jones [3] in this country, who have pointed out that probably its most important object is the digestion and removal of the elastin fibres, which are very abundant in the grain layer (p. 63) and prevent its stretching. Figs. 40–43 are from photographs by Mr Guido Daub of Messrs Galluns' laboratory of Milwaukee, and are sent by Mr J. Wilson, their chief chemist.

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[1] *J.A.L.C.A.*, 1916, p. 463; *J. Ind. Eng. Chem.*, 1920, p. 1087; *J.S.L.T.C.*, 1921, p. 15.

[2] *Collegium*, 1918, pp. 108 and 125.

[3] *J.S.L.T.C.*, 1920, p. 60.

Seymour-Jones has also shown that in some cases it is sufficient merely to paint the grain with the enzyme-bate, without acting on the fibrous part of the corium, which contains little or no elastin.

In addition to the artificial bates which depend on the pancreatic enzyme, a considerable number of preparations of a secret nature are on the market, most of which are drenches or deliming agents rather than true bates, though for certain classes of leather they may serve a useful purpose. Many of them contain glucose or sugars, and some lactic or butyric ferment. Perhaps an exception should be made to a patent by the late Dr Eberle of Stuttgart,[1] who employs gall and extracts of the intestines in addition to the pancreatic ferments. These contain enzymes which activate the trypsin and steapsin, and so render

Fig. 40.—Butt of calfskin bated with ammonium chloride only. Elastin stained with Weigert's magenta.

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[1] Eng. Pat. 21,202, 1909.

the addition of ammonium salts unnecessary. A good deal of detail about this and the other advertised bates will be found in Wood's *Puering, Bating, etc.*, chapter viii.

As the old-fashioned puering method with dog-dung is still in considerable use, some further details of its action are necessary.

From the multiplicity of germs present, and the adaptability of the dung infusion as a nutrient medium for any putrefactive organisms which may gain access to it, the bating and puering process is necessarily a dangerous one for the goods, always leading to loss of weight, and, if the process is carried on too long, to the more or less complete destruction of the skins. Loss of weight, however, in greater or lesser degree, is inevitable, and indeed necessary where a soft leather is to be produced. If the skins are allowed to lie in the bate or puer liquor, mud, containing organisms, and zooglœa-forms of bacteria settle in the folds, and

FIG. 41.—Butt of calf-skin after six hours' bating with trypsin. Stained as before.

produce marbled markings, streaks, and lines by the destruction of the grain surface (hyaline layer). Black or bluish stains are also often produced, known as bate-stains, and are either due to bacterial pigments or, in some cases, to the action of evolved hydrogen sulphide on iron present from salting or other sources. Frequent change of position is therefore necessary, especially when the liquor is active from being used at a high temperature, but it does not seem to be desirable to keep the skins in constant motion, as "weak grain" may be produced by the mechanical friction, and if puering is done in a paddle, it should only be run at intervals.

FIG. 42.—Butt of calf-skin after twenty hours' bating with trypsin. Stained as before.

T. Palmer [1] determined in experiments on pigeon-dung bates that there is considerable loss of nitrogen during the process, and recommended bating in pits from which the air was excluded

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[1] *Leather Trade Circular*, 22nd Sept. 1891; 1887, p. 667; and Sanford, *Journ. Soc. Chem. Ind.*, 1893, p. 530.

as much as possible, both as effecting a considerable economy in the dung and in excluding false ferments, which, he concludes, are mostly aerobic. It is not improbable that the method is advantageous, since it has been shown by Roscoe and Scudder that liquefaction of gelatin only takes place in presence of oxygen, and its partial exclusion would therefore lessen the risk of over-bating, and consequent damage and loss of weight.

FIG. 43.—Butt of calf-skin after twenty-four hours' bating with trypsin. Stained as before.

Starting from the presumption that bating and puering are, in the main, bacterial processes, more or less successful attempts had been made previous to those of Wood, Popp and Becker, to substitute other fermenting substances for dung ; and probably these efforts failed in many cases, not so much because they were wrong in principle as from want of knowledge of the necessary details, such as the use of proper ferments, and the provision of suitable culture-media. Guano, prepared horse-flesh, urine, yeast, and fermenting vegetables have all been tried. A solution of glucose or treacle of about 10 per cent., to which 3 per cent. of pasty dog-puer is added about a week before use, was tried many years since in a morocco factory, at the suggestion of the writer, as at least a partial substitute for puer, and remained long in use there. The mixture kept for some time in an active state, and was added to the puer liquors in the same way and in approximately the same proportions as the dung paste. Similar in principle was the solid bate supplied by an American firm, in which glucose was mixed with a small amount of nitrogenous matter and phosphates, together with a lactic ferment, and which only requires dissolving in warm water some little time before use. Its results were good for some purposes, but rather resembled those of a drench than a bate. In a similar way, puer may be added to bran-drench liquors, and induces in them a fermentation which brings the skins down much lower than the ordinary drench. It is probable that a weak glucose solution, with traces of mineral constituents similar to Cohn's solution (see *L.I.L.B.*, p. 269) and " set " with sour milk or fermenting drench-liquor, might in some cases be used with advantage for drenching, with a saving of cost. A writer in *Hide and Leather* describes a bate in which 2 parts by weight of glucose are dissolved in about 25 parts of water, and fermented, for about three days, with about 1 part of old bran drench-liquor, or 0·1 part of pressed yeast, till a foam gathers on the top, and then made up with water to 1000 parts; the goods bated twenty-four to thirty-six hours at a temperature of about 35° C., and the bate strengthened for a second pack with about one-fifth of the original glucose, a new bate being made at the end of a week and set with one part per thousand of the old one. A short bating of, say, ten hours produced very nice harness leather, but the general tendency was to make the goods looser and more spongy than a dung-bate. It is obviously not a matter of indifference whether old drench or yeast is used to start the fermentation, since in the latter case only alcohol could be produced directly by the ferment introduced, though this might be fermented later by other accidental organisms into acetic acid. These mixed bates containing glucose are, however, probably wrong in principle, since the true puering and bating bacteria will not thrive in presence of acids and require nitrogenous nutriment, and if such bates are serviceable at all, they act as drenches rather than as true bates.

As regards the relative effect of dog- and hen- or pigeon-dung bates, the chief of the published experiments are those made by W. J. Salomon at the Vienna Versuchsanstalt für Lederindustrie,[1]

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[1] *Tech. Quart.*, 1892, v. p. 81.

in which he determined the relative solvent power of equal quantities as being, for dog-dung 2½, for pigeon-dung 2, and for hen-dung 1. It is obvious that these figures, though interesting, must be taken with some reserve, as the composition even of pure dungs is by no means constant, depending on the feeding of the animals, and adulteration is common. The writer has heard stories of a certain dealer who used to fabricate his product from clay by the aid of a popgun, though he does not vouch for the statement! It is generally held that the action of bird-dung is more penetrating but less softening and loosening than that of dog-dung, which is thus generally used for descriptions of leather where great softness and stretch are required. It is to be remembered in this connection that bird-dung bates are generally used cold, and hence are much slower in their action, which allows them time to penetrate thicker hides more uniformly. Few analyses of the dungs used in leather manufacture have been published, and these mostly with a view to manurial value. Schulze[1] gives the result of forty analyses of pigeon-dung as follows:—

	Min. Per cent.	Max. Per cent.	Mean. Per cent.
Water	3·80	40·00	21·00
Nitrogen	1·47	5·04	2·53
Phosphoric acid	1·00	2·77	1·79
Potash	0·71	2·57	1·46

One sample contained 43·3 per cent. of sand!

Wood[2] quotes the following:—

Hen-dung.	Per cent.
Water	60·88
Organic matter[3]	19·22
Phosphates	4·47
Calcium carbonate and sulphate	7·85
Alkaline salts	1·09
Silica and sand	6·69

Dog-dung.	
Water	31·0
Ca	43·0
Na, K, Mg	0·8
PO_4	3·4
CO_2	7·5
Organic matter	14·2
Traces Fe, Cl, Si, loss	0·1

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[1] *Der Landwirt*, 1895, li. p. 301.

[2] *Journ. Soc. Chem. Ind.*, 1894, p. 220.

[3] Containing nitrogen equal to 0·74 per cent. of ammonia.

This was apparently a sample from a dog fed on bones; that from the kennels, which is more commonly used in leather manufacture, contains much less lime; a sample analysed by Wood gave 4·7 per cent. mineral matter, 9·7 per cent. organic, and 85·6 per cent. of water, part of which was no doubt added.

The quantity of hen- or pigeon-dung used in bating hides is very variable, but may be stated at from 12 to 60 litres per 1000 kilos. of raw hide in at least 2000 litres of water. The bate is generally used cold, the hides remaining in it four to eight days, with frequent handling; but some tanners, especially in the United States, prefer bating in a paddle or drum at a temperature of about 35° C., in which case the time must be diminished to a few hours. The dung is best infused with warm water in a separate vessel[1] and allowed to ferment for at least a week without use, when it will be found to swarm with micrococcus-chains. Only the clear liquor should be run into the bate-pit, the sediment and dirt being thrown away or used as manure. In this way the danger of stains and flaking is much reduced. Bates may be mended with fresh portions of dung-infusion for several successive packs of hides, but should not be used too long, as they gain in solvent power by the dissolved hide-substance and the increased fermentation, and the method is not without risk.

After bating the hides are usually "worked" ("scudded," "fine-haired") on the beam to remove dirt and grease, but in America a wash in the wash-wheel is often considered sufficient. Goods are occasionally "stocked" (p. 163) from the bates, but this is not to be recommended, as it is likely to drive out much of the partially dissolved hide-substance and produce undue looseness and loss of weight.

It is difficult to give any definite marks of sufficient bating other than the soft and fallen feel of the hides, which is easily recognised by a practised hand. One of the earliest signs of commencing overbating is the occurrence of bluish patches or a bluish tinge somewhat similar to an iron-stain, which, if slight, generally disappears in a few days after the hides are taken into the liquors. Hen- and pigeon-dung is probably best kept air-dried, though, if very wet, or for convenience for immediate use, it may be kept in paste like dog-dung.

Dog-dung should never be allowed to lie exposed to the air, or it putrefies and turns black, the bating ingredients are destroyed, and it will not puer the goods, which turn black and putrid without softening. Dung should, therefore, be mixed to

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[1] This seems to have been first suggested by T. Palmer, Eng. Pat. 13,636, 1886.

a paste with water and kept in tanks so as to be but little exposed to the air, when it will retain its puering properties for a long time unaffected. Fresh dung should be allowed to ferment for at least a week before use. No accurate statement can be made as to the quantities required. Eitner states that 1 to 1½ pails of dung-paste (say 14 to 20 litres) is sufficient for 200 medium to large lamb-skins for glove-kid. It should be sufficient to make the water quite turbid, but not thick or soupy. For lamb-skins a temperature of 18° to 20° C. is suitable, which may be raised in very cold weather to 25° C. to allow for cooling. The time required is from two hours for the thinnest slink skins, to twelve to fourteen hours for strong ones. It is well to use wooden, and not iron, utensils for handling the dung, and it should be strained through a coarse cloth after diluting with water. As has been remarked, it is not desirable to keep the skins in constant motion in the puer; they should be stirred or paddled for the first twenty to thirty minutes, and then for ten minutes every hour for five or six hours, after which they can be allowed to lie for a longer period without injury. Puering is sufficient when the skins feel quite soft and flaccid, hanging in folds in any direction and allowing the flesh to be scraped off with the finger-nail.

Wood recommends that for the puering of sheep-skins dung should be allowed to ferment one month before use, and states that it deteriorates if kept over three months. The puering products are the result of the successive action of many sorts of bacteria, and Wood is of opinion that those actually concerned in puering originate from the air, or from the vessels in which the dung is stored, and are not present in it when excreted. Borgman[1] advises that the dung should be kept in a dry condition, and only made into a paste between a fortnight and three weeks before use by covering in a clean cask with cold water, and on the following day mixing to a smooth paste with a clean wooden "poss-stick," made from wood free from tannin. The cask should then be covered up, and allowed to rest undisturbed till required. Clean extract-casks are very suitable for the purpose if carefully and repeatedly steamed out, and Borgman advises that a regular series should be arranged so as to supply the dung required, the date of mixing being carefully marked on each cask. Throughout the process the utmost cleanliness should be observed, and the casks should be carefully steamed out as soon as emptied. Immediately before use the dung-paste should be heated by steaming nearly but not quite to boiling

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[1] *Die Feinleder-Fabrikation*, Berlin, 1901, p. 69.

point,[1] care being taken to avoid the introduction of condensed water containing iron, and the dung thoroughly mixed with a large quantity (say 100 gallons) of water at 45° to 50° C., allowed to settle, and drawn off through a basket, and strained into the puering paddle through a second basket lined with coarse open canvas (such as is used by plasterers to cover windows while the plaster is drying). A further quantity of warm water should be poured on the residue in the mixing tub and used for diluting that in the paddle to the proper volume. The temperature of the liquor may reach 42° C. before the skins are introduced. The liquor should be of a light colour, greenish to brownish-yellow; if darker, it indicates decomposition of the dung by improper storing or too long fermentation, and will be liable to cause staining and injury to the skins. About 33 litres of dry dung is required per 100 kilos. of wet skin prepared for puering (33 gallons per 1000 lb.). Dry dung should be of yellow to brown colour; dark brown or black dung is spoiled and unsuitable for use. Wet dung is more difficult to judge, but very dark brown or black should be rejected, as well as that with a very strong smell, indicating that it has already fermented. Borgman's directions bear the stamp of experience and common sense, and the book as a whole repays study.

Borgman recommends that the skins should be warmed by paddling for some time in water of about 40° C., to which a couple of pails of puer-paste have been added, before bringing them into the puer, the temperature of which they should reduce to perhaps 38° C. The puered skins should feel silky on the grain, and even somewhat slippery, and when pressed between the finger and thumb a dark impress should be left, and the flesh should be tender and easily scraped off. The requisite condition will, however, vary somewhat with the kind of skins and the purpose for which they are intended. After puering, the skins may be paddled for half an hour in water of about the same temperature as the puer.

The only attempt of which the writer is aware to give an actual mechanical and numerical value to the effect on the skin of puering and deliming processes is that of Wood, who, in collaboration with Dr H. Sand and D. J. Law, constructed an instrument for measuring the exact compression and elasticity of the skin under varying loads.[2] For full details the original papers must be consulted, but the following brief description may be

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[1] This seems a dangerously high temperature, both for enzymes and bacteria.

[2] The "puerometer." *Puering, Bating, etc.*, p. 85; *J.S.C.I.*, 1913, p. 398.

given here. The apparatus consists of two discs of about 1 cm.^{2} area, the upper of which is attached to a long balanced arm, which is loaded by means of a sliding weight on the principle of the steelyard, and of which the exact horizontality is determined by means of an electric contact device. The lower disc rests on a micrometer screw, by which the thickness of the skin can be determined when it is pressed against the upper disc to such an extent as to exactly balance the load. With small loads gelatin is perfectly elastic, returning to its original thickness when the load is released, and this is also the case to a large extent with skin still swollen with lime, but in the delimed or puered skin this resiliency is greatly diminished, while the compressibility is increased. The apparatus is of considerable value as giving a numerical value for the puering, which can be referred to and repeated at any time, but the conditions are too complex for it to be easy to draw theoretical conclusions from the results. The skin consists of a mass of gelatinous fibres, much swollen themselves in the limed condition, but with some water between them, while when puered the fibres are much less swollen, but with a larger proportion of water in the interstices. The fibres themselves, especially when swollen, have also a certain degree of rigidity ; and all jellies, like indiarubber, oppose an elastic resistance to change of shape. When a piece of skin is compressed between two discs all these forces come into play in varying proportions, but any real compression of the water itself or of the actual skin-substance is quite negligible. The first effect, especially on puered skin, is to expel the water from the interstices between the fibres, but if the pressure is sufficient to overcome the osmotic force which produces swelling (see Chapter X.), it is also expelled from the fibres themselves, and this required pressure will be affected by temperature and by the degree of alkalinity of the fibre. If jelly is compressed between the discs it will bulge round the edges, and the degree to which this occurs will of course depend on the relative size and thickness of the compressed jelly. The time-element must also be considered, especially as regards resilience, as most of these effects depend on the flow of water through the skin, where it meets with great frictional resistance, and the comparatively small forces tending to restore equilibrium must necessarily take time to act. Rapid resilience probably depends mostly on the mere deformation of shape of the jelly-fibres or of the mass of jelly.

CHAPTER XV

PICKLING AND DEPICKLING

THE process of pickling, though long used for the preservation of untanned pelts, has become of increased importance from its extensive use as a preparation for chrome tanning, and much light has been thrown on its principles by the researches of Procter and Wilson, so that it seems to demand a short chapter to itself.

The general process consists in the swelling of pelt with an acid, and then treating it with a strong solution of common salt, in which the swelling entirely disappears, and the pelt becomes very flat and thin, and is in fact converted into a sort of white leather, which, however, at once swells again if placed in water. The principles of the process are adequately explained in Chapter X., and need not be here repeated; but it is highly probable that in addition to the disappearance of the swelling osmotic pressure there described, an actual "salting out" by the very strong salt-solution occurs, which has not been completely explained, but which may be either due to the consumption of the solvent in hydrating the unionised salt, or to the jelly becoming impermeable to the solution of the unionised salt, and so experiencing the whole instead of only a small fraction of the outside osmotic pressure. There is little doubt that this is the explanation of the powerful effect of anhydrous alcohol mentioned on p. 586, and there are neutral salts, especially ammonium sulphate, which will salt out neutral gelatin and pickle skin, with regard to which ionisation can hardly come in as an explanation.

The earlier mode of pickling was to swell (and incidentally to "tuck up") the skins in sulphuric acid much diluted and then to bring them down in strong salt solution, but it is now universal to add some salt also to the "rising solution" itself to control undue swelling. A suitable strength for the rising solution is about 80 grm. common salt and 7·5 grm. sulphuric acid per litre.[1] One hundred c.c. of this solution will require about 15 c.c. of N/1 alkali to neutralise it, and it should be tested after each lot of skins, which should weigh when wet about 660 grm. per litre of solution, and maintained at the same strength by

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[1] This is at the rate of 80 lb. of salt and 7·5 lb. of sulphuric acid per 100 gallons, or the same number of ounces per cubic foot (*cp.* p. 581).

suitable additions of acid. The bath should fall during use to a strength requiring about 7·5 c.c. of N/1 alkali for neutralisation of 100 c.c., and, if necessary, the strength of the original acid should be diminished, or the time in the bath should be adjusted so that this occurs.

A much weaker solution of acid than the above is sufficient for adequate pickling, and a more satisfactory pelt results. The writer once experimented with one-tenth of this acid, and the skins kept perfectly, but a longer time in the bath is required, which is inconvenient commercially. The acid absorbed by the skins is mainly hydrochloric, sodium sulphate accumulating in the bath. The salt is not absorbed by the skins in the same way as the acid, but will be continually diluted by the water they bring in, and occasional additions of salt must therefore be made, the density being maintained at about 65° Bkr. (1·065 sp. gr.). After paddling or being stirred in this bath for about ½ or ¾ hour the skins are transferred to saturated brine, and stirred in it till fully fallen in thickness, the density of the liquid being maintained by excess of salt. They may be allowed to remain some hours in the saturated brine with advantage.

Within moderate limits the strength of the rising liquor is not of great importance, since the skins will only absorb a certain amount of acid (increasing with the concentration of salt). In the second or falling liquor the large excess of salt forces all the acid present into the skins, none diffusing into the bath. Skins may be effectively pickled with very much smaller quantities of acid than those prescribed above or ordinarily used, and are much easier to tan satisfactorily, but it is said that they are more liable to suffer from mildew.[1] Pickling may also be done by placing the skins in a concentrated brine-bath and adding a

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[1] Hydrochloric acid in equivalent proportions may be substituted for sulphuric, and has been said to prevent mildew and other fungoid trouble, which sometimes occur with pickled skins, but both this and the statement that skins pickled with little acid are more liable to mildew is open to much doubt, as tanners are prone to attribute to any new method troubles which are really due to faulty manipulation or some accidental cause. Sulphuric acid and salt are generally cheaper than hydrochloric acid, and in either case it is hydrochloric acid which is absorbed by the skin, but if the former mixture is used, and skins are not thoroughly freed from lime by previous deliming, a certain amount of calcium sulphate may be precipitated in the skins, and this has been shown in the case of salt-stains (p. 37) to favour some sorts of bacterial activity. Many of the troubles which occur in pickling are not due to the particular acid used, but to its careless use, and in particular to the rough way in which it is generally measured.

calculated quantity of acid, not exceeding about 1 grm.-molecule of sulphuric acid per kilo. of dry hide-substance, but the method is not economical in practice, from the dilution of the bath produced by the water brought in by the skins and the necessity of constant large additions of salt.

Pickled skins must not be brought into contact with water, which, by diluting the brine they contain, allows the excess of acid to act upon and destroy the fibre. Even drops of water accidentally sprinkled on the skins produce this effect, and it is said that it spreads to parts which have not been wet. For similar reasons it is necessary in tanning pickled skins at least to begin the process in liquors to which salt has been added, the quantity required being dependent on the amount of acid used in pickling the skins, and where this is reduced to a minimum, it is even possible to tan without further addition of salt than that contained in the skins.

In place of mineral acids, organic acids such as formic and acetic might be substituted with great advantage as regards safety and easy subsequent tannage, but would be much more expensive, but in some cases they certainly deserve attention. Formic acid especially has itself strong germicidal properties. Some years ago Mr A. Seymour-Jones pickled sheep pelts with formic acid and salt, and sent them in a light box up the Amazon to Manaos and back, and they arrived again in England in a perfect condition, spite of the fact that the voyage was through one of the most trying regions of the Tropics.[1] The Seymour-Jones process for sterilisation of skins against anthrax is also a formic acid pickling, and the addition of the small percentage of mercuric chloride practically guarantees not only against anthrax, but against moulds and mildew. To sterilise dried hides they are soaked for twenty-four hours in a solution of 1 per cent. of commercial 90 per cent. formic acid and 0·0002 per cent. of mercuric chloride, and for skins a less concentration of formic acid has proved efficient. For pickling the actual concentration is not so important as that the acid absorbed should be about 4·5 per cent. on the actual dry hide-substance of the skin. After the acid treatment the skins or hides are treated with saturated salt solution as usual, or even salted with dry salt.

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[1] *Colleg.*, 3, 1904, p. 186. Seymour-Jones recommends for skins after deliming and drenching a treatment for twenty-four hours in a 0·25 per cent. solution of formic or a 1 or 2 per cent. solution of "pyroligneous" (crude acetic) acid free from iron in a paddle which should be run for a few hours at first. They should also remain twenty-four hours in the saturated salt solution.

The writer found by analysis of skin treated in this way, that after the salting the formic acid was practically entirely replaced in the skin by hydrochloric. It may seem rather strange at first sight that the weaker formic acid in the hide should have been able to liberate and take up the hydrochloric from the salt, but the result follows from the mass-law. In treating with a very large excess of salt the Cl ions are in enormous excess, and the result is the formation of a very minute quantity of gelatin formate and a comparatively large quantity of gelatin chloride, and a similar distribution of the sodium salts.[1] It is therefore probable that the process might be cheapened without disadvantage by employing about 3 per cent. of HCl and only 1 per cent. of formic acid on the actual dry material of the skin. This would correspond to, say, 2 per cent. of ordinary commercial hydrochloric acid on the wet weight of pelt, and it might be advisable to add, say, 0·2 per cent. of formic acid to the final salt solution rather than mix it with the HCl of the rising solution.

Several methods of pickling have been suggested which do not involve the use of acids. Meunier proposes to treat with a dilute solution of bleaching powder, and also with saturated solution of potassium carbonate (*cp.* p. 575), but both of these methods have disadvantages which tell against their practical use. It has also been mentioned that skins could be dehydrated and preserved by soaking in saturated solutions of ammonium sulphate, but the ordinary commercial article contains phenolic or tarry impurities, which produce an actual tannage of the skin, and prevent its returning to pelt on soaking (*cp.* p. 576).

Skins pickled with acids, and especially with the stronger acids, still retain enough to cause them to swell excessively if soaked in water so as to remove the salt, and if tanned in this state produce with vegetable tans a quite rotten leather. The usual remedy is to add sufficient salt to the early liquors to prevent swelling until the acid of the skins has been sufficiently displaced by tannin, and in America it is not unusual not only to add salt but actually sulphuric acid to sumach liquors in the first stages of tanning, which produces leather with a very much smaller expenditure of sumach than in the normal process. The leather is apparently fully tanned, and does not appear to contain free sulphuric acid, which is probably expelled by the tannin in the later stages of the process.

When it is desired to give a normal tannage without salt the skin must be first "depickled," that is, the acid must be neutralised or removed. This may be done by any weak alkaline solution,

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[1] *Colleg.*, 11, 1912, p. 687.

but considerable care is required not to bring the skin into a really alkaline condition. The prettiest process, theoretically, is to drum or paddle with an insoluble alkaline carbonate, such as "whitening," or with magnesia, but it has the evil in practice that some of the whitening is apt to adhere mechanically to the skin and produce stains or bad colour. Sodium bicarbonate or borax are suitable salts to use, but excess must be avoided, and ordinary soda crystals may be used satisfactorily with sufficient care. No doubt Stiasny's neutralising mixture (p. 272) of soda crystals and ammonium sulphate or chloride in about equal quantities would also be safe and efficient. One of the cheapest and most satisfactory depicklers is sodium thiosulphate (" hypo "), as recommended by Mr Seymour-Jones,[1] as it is quite neutral, and cannot do injury by excess.

When pickling is used as a preliminary to chrome tannage, the object is quite different from that of its use as a preservative, and is generally to introduce acid into the pelt. Thus if a heavily pickled pelt be introduced into a neutral bichromate solution it will be depickled by the action of the bichromate, and sufficient chromic acid will be liberated to chrome the skin, and in any case a much smaller amount of acid will be needed in the chroming

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[1] *Colleg.*, 11, 1912, p. 620. Seymour-Jones uses 4 to 5 lb. per dozen pelts. He also mentions a variety of other uses to which thiosulphate can be put in leather manufacture. Finely ground hypo can be used in place of salt as a preservative of hides and skins. It is a powerful dehydrant, and if prepared pelt is saturated with hypo and then treated with a weak acid, a beautiful white leather results, partly by dehydration, and partly from the finely precipitated sulphur, which can be fat-liquored and dyed, or, treated with suitable oils, will produce a sort of chamois-leather. Instead of an acid, alum or aluminium sulphate can be used to decompose the hypo and give an alumina tannage, and if formaldehyde be further added, a good buff-leather results. A curious and unexplained effect is the removal of grease and fat from pelt or leather. If greasy hides or skins are delimed by saturated hypo solution and treated with a weak acid bath, or cleansed skins are slightly swollen with acid and then treated with hypo, in either case in a paddle or drum, the grease can be worked out on the beam, or the skins may be chromed without the grease subsequently appearing.

Greasy butts after rolling may be suspended in a 10 to 20 per cent. solution of hypo at 140° Fahr. for a few hours, when the grease will float to the surface, and should be skimmed off before the butts are withdrawn. If subsequently treated with a weak acid, preferably formic, the colour will be much improved, but a good deal of tan will be stripped, and if used for sole the leather will require re-tannage. Hypo can also be used as a bleaching agent for extracts, and if hides are treated with from $2\frac{1}{2}$ to 10 per cent. of hypo they may be drum-tanned with neat extract in a very short time.

bath than with unpickled skins (see p. 261). For the basic process pickling is also often useful, as enabling a much more basic liquor to be used at the outset without precipitation or "case-hardening" the skin, so that a heavier tannage can be given to the interior without overtanning the outside.

For these purposes it is obviously unnecessary to treat with a saturated salt-bath after "rising," and it will generally be better to add such an amount of salt to the rising liquor as will prevent more swelling than is desired. Instead of free acid, alum or sulphate of alumina is often used with or without salt, giving a certain amount of preliminary alumina tannage.

Seeing that the objects of this preliminary pickling vary so much, it is impossible to give definite quantities or directions, as it really forms a part of the subsequent tanning process, to which it must be adapted.

CHAPTER XVI

ALUM TANNAGE OR TAWING

We have now followed the raw material up to the final stage of preparation for its actual conversion into leather, and it remains to consider the means by which that important change is produced. Though as yet the vegetable tanning process is most largely used, and possesses the greatest commercial importance, the use of mineral salts has long been known, and, through the advent of chrome tanning, has placed the permanent supremacy of the vegetable tannins in considerable doubt. Not only the importance of mineral tanning processes, but their greater simplicity from the scientific side, justifies their consideration before those of vegetable origin.

In the previous chapters it has been shown that to produce a permanent leather it is not only necessary to dry the fibres in a separate and non-adherent condition, but so to coat them or alter their chemical character that they are no longer capable of being swelled and rendered sticky by water. All salts (see p. 123) which produce a contraction or dehydration of the fibre similar to that caused by alcohol are capable of the first effect in a greater or less degree. Many sulphates, and particularly those of sodium and magnesium, though they will not alone produce leather, will so far contract the fibres as to greatly hasten tanning by vegetable tanning materials, and they are therefore capable of useful application in quick-tanning processes, especially where tough and light-weighing leathers are aimed at, which may be subsequently weighted and solidified by further treatment. Strong solutions of ammonium sulphate are almost as strongly dehydrating as alcohol, and will produce white leathers very similar to those formed by pickling, a fact which is certainly of considerable commercial importance. None of these salts, however, can form a complete leather in themselves, but require the assistance of metallic salts, which will permanently fix themselves in the fibre, and diminish or destroy its attraction for water. Many substances have this power in a greater or less degree, but all those of commercial importance belong to the group of which aluminium, iron, and chromium are representative, and which are capable of producing salt-forming oxides of the formula M_2O_3 (*e.g.* alumina,

Al_2O_3). Manganese, of which the salts of this type are very unstable, has very slight tanning power, while titanium, which in many ways is allied to the group, though it does not strictly belong to it, has recently been patented as a tanning agent. For the present, however, we may limit our attention to the three metals first named.

Alumina and its salts demand the first attention, not only as having been used for leather manufacture in very early times, but as being still important commercially. The metal aluminium is now well known, and its oxide, alumina, Al_2O_3, is abundant in Nature, combined with silica in the form of clay and bauxite, as fluoride in combination with sodium fluoride in cryolite, and in some cases as a native sulphate. Alum-shale, which was formerly the principal source of alum, is a bituminous clay containing much iron sulphide, and which when calcined yields aluminium sulphate. As aluminium sulphate does not crystallise readily, and was difficult to free from iron, potassium sulphate was added to the liquor obtained by leaching the calcined shale, from which, after concentration by boiling, a double sulphate of potassium and aluminium, $Al_2(SO_4)_3,K_2SO_4,24Aq$, potash-alum, was easily crystallised out. Alum is now usually made by decomposing clay or bauxite with sulphuric acid, and ammonium sulphate is generally substituted for the potassium salt, yielding ammonia-alum, a double sulphate of aluminium and ammonium of similar constitution to potash-alum. Ammonium alum is easily distinguished from the potassium salt by the strong smell of ammonia which it evolves on the addition of caustic soda or lime. So far as is known there is no practical difference in tanning effect between the two salts, and ammonium alum is cheaper, and slightly stronger, its molecular weight being 906, as against 948 for the potassium salt. Either alum dissolves readily in cold water to the extent of about 9 parts in 100 of water, and more easily, and to a much larger extent, in hot water, from which the excess crystallises on cooling. It is said that for purposes of leather manufacture alum solutions should not be boiled, and, though it is improbable that this produces any considerable change, it must be remembered that chrome alum on boiling really does undergo decomposition to free acid and a more basic salt, indicated by change of colour from violet to green, from which it slowly returns to the violet form on cooling.

Alums are only valuable in leather manufacture in proportion to the aluminium sulphate which they contain, the potassium or ammonium sulphate taking no part in the reaction except as a "neutral salt" (p. 123), and since improved methods have rendered possible the production of aluminium sulphate practically free from iron, it has largely taken the place of alum, than which it is both cheaper and stronger. Crystallised aluminium sulphate, $Al_2(SO_4)_3,18Aq$, has a molecular weight of 666, and is of equal value to 906 of ammonia-alum and 948 of potash-alum. Iron is the most objectionable impurity in both alums and aluminium sulphate, and may be detected by the addition of potassium thiocyanate, which will produce a red colour, or potassium ferrocyanide ("yellow prussiate of potash"), which will produce a blue. As the iron may be present in the ferrous condition, it is safer to add a little ferricyanide ("red prussiate"), or first to boil the alum solution with a few drops of nitric acid or bromine water. For more accurate determination of iron see *L.I.L.B.*, pp. 20, 136.

No satisfactory leather can be produced with a solution of alum or aluminium sulphate alone, the skin drying horny, and incapable of softening by stretching. In practice, salt is always used in addition, the proportion being very variable, but averaging about half the weight of alum, or two-thirds the weight of sulphate of alumina employed. The mode of action of the salt has long puzzled chemists, and it has been supposed that its use was to convert the aluminium sulphate into chloride, a reaction which takes place to some extent, but which fails to explain the production of a soft leather, since aluminium chloride, though freely taken up by the skin, produces alone no more satisfactory leather than aluminium sulphate. The real explanation is found in Chapter X. Alumina is a weak base, which readily gives up its acid to the pelt, becoming converted into a basic salt (see below). The acid not only swells the pelt and renders it incapable of producing a soft leather, but the swollen pelt is less ready to absorb the alumina salt, and so remains undertanned. The addition of salt prevents the swelling effect of the acid, and produces a partial pickling of the skin (p. 234), which, in conjunction with the tanning effect of the basic alumina salt formed, yields a satisfactory leather, though one which is readily affected by washing. If instead of adding common salt to the alum solution, an alkali such as soda is added, it combines with a portion of the acid, forming sodium sulphate, while the alumina remains in solution as a "basic salt." As the term "basic salt" must be frequently employed in connection with mineral tannage, it may here be explained. Basic salts are compounds intermediate between the normal salt, in which the whole of the base is combined with acid, and the hydrated oxide, in which the whole is combined with OH groups. Thus aluminium chloride,

Al_2Cl_6, is a normal salt, in which the whole of the three combining powers of the aluminium are saturated with chlorine ; aluminium hydrate, $Al_2(OH)_6$, is the hydrated oxide, and Al_2Cl_5OH, $Al_2Cl_4(OH)_2$, and so on are basic salts, in which successively more of the Cl is substituted by OH. It is somewhat doubtful, however, whether most basic salts are really definite compounds, and not rather, colloid solutions of the hydrate in the normal salt. Generally, as a salt becomes more basic its solution in water becomes more unstable, and very basic salts are either insoluble, or are precipitated from their solutions by very trifling causes, such as boiling, dilution, or the attraction of animal or vegetable fibres, separating into free acid and either hydrate or a still more basic and insoluble salt. On this property depends their importance in tanning and dyeing, many of the metallic mordants being solutions of basic salts. Basic salt solutions are formed in various ways, the most common being the direct solution of a hydrated oxide in a solution of the normal salt, or the neutralisation of a part of the acid of the normal salt by the addition of a stronger base. The latter takes place on the addition of soda to an alum solution. If the soda is added in excess, the whole of the alumina is precipitated as hydrate, or as an insoluble basic salt, but if a proportion not exceeding about four parts of crystallised sodium carbonate be dissolved separately, and added *slowly with constant stirring* to the ten parts of alum dissolved in water, no precipitation will take place. In this solution leather can be tanned, either with or without addition of salt, the alumina is taken up more freely than from the normal alum, and the leather is more easily softened, and more resistant to water. In fact such leather bears a strong resemblance to the chrome tannages, standing a great deal of washing and considerable temperatures without returning to a pelty condition. The more basic the solution that is used, the fuller and softer is the leather produced. The alumina-salt taken up by the skin from such basic solutions is always basic, while that absorbed from alum or alumina sulphate is *apparently* the normal aluminium sulphate. It is probable, however, that the actual tanning salt is in both cases basic, and that the acid is fixed as free acid, as in the pickling process, as the proportions of acid and base found in the residual liquor are somewhat variable. The basic salts will be more fully discussed in relation to chromium and iron in Chapter XVII., where they are of greater importance.

Basic alumina solutions have hardly taken the place in practice which they deserve, though they were described by Knapp in

1858 [1] and have since been patented by Hunt, but the patent (probably invalid) has long lapsed. A good stock solution for practical use is made by dissolving 10 lb. of sulphate of alumina in 10 gallons of water, and 4 lb. of washing soda in 4 gallons, and gradually mixing the latter with the former. Salt can be used in addition if desired, and flour and egg-yolk may also be added. Basic alumina solutions can also be used in considerable quantities in conjunction with chrome, without rendering the leather incapable of standing the boiling test, or materially altering its colour.

In curing small skins, where it is not desirable for the fur to come in contact with the liquid, or in the tawing of wool rugs, it is often convenient, after freeing the skin as much as possible from blood and dirt and adhering flesh, to stretch it on a frame, or nail it out on a board, and apply a strong alum-and-salt solution, as hot as the hand will bear, with a sponge, repeating the operation till the skin is struck through.[2] About 1 lb. of alum and ½ lb. of salt per gallon is a suitable strength. In place of applying the solution, powdered alum and salt is sometimes rubbed into the wet skin. Alumed goods should generally be dried out rapidly, and finally at a good temperature, as this tends to fix the tannage, which is also made more permanent and resistant to water by keeping the skins for a month or more in the alumed condition, an operation known as "ageing." When first dried, alumed goods are invariably stiff and horny, and, to give them softness, must first be damped back to a flexible condition (best by placing in slightly damp sawdust), and then gradually softened by mechanical means. "Staking" and "perching" are the usual methods, the first consisting in drawing the goods vigorously over a bluntish blade fixed on the top of a post, and the second in fixing the skins on a horizontal pole (the "perch"), and working them with the "crutch stake," a tool formed somewhat like a small shovel with a semicircular blade, in place of which a "moon-knife" (a round blade somewhat like a broad thin quoit) is often fixed in a wooden crutch. The tools and mode of using them are shown in figs. 44 and 45.[3]

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[1] *Natur und Wesen der Gerberei*, Braunschweig, 1858.

[2] A similar method can be used with strong basic chrome solutions, producing a leather which can be washed, and if the solution be saturated with salt, and allowed to dry on the skin before washing, the crystallisation of the salt so softens the skin as to render staking almost unnecessary.

[3] The process shown in fig. 45 is not actually "perching," but "grounding," in which a moon-knife with a sharp turned edge is used to reduce the thickness of the skin on the perch, at the same time as it stretches and softens it, but the action is much the same.

Machines, described on p. 248, are now generally used for these operations. After the first staking or softening the skins are allowed to become nearly dry, and are then staked a second time. Some judgment is required as to the precise degree of moisture in each case: in the first instance the skins must be sufficiently damp to yield without injury to the mechanical stretching, but in this state they retain sufficient moisture to enable the fibres again to adhere on drying; and at the second staking or perching they must be damp enough to allow these fibres to be loosened without violence, and dry enough to prevent their again adhering. The first stretching must not be too severe.

FIG. 44.—Staking White Leather.

The following slight sketch of the manufacture of calf-kid will serve to illustrate the practical manufacture of the finer alumed or "white" leathers, though little if any is now made. The raw material is in England mostly large market-calf, though salted and dried skins are sometimes employed. After sufficient soaking or washing in water they are limed without arsenic or other sulphides, in limes which must not be allowed to grow stale or putrid, until the hair can be easily removed. After unhairing and fleshing in the usual way they receive a few days in a pretty fresh lime in order to plump them, and are then freed from lime gradually, but as completely as possible, by successive steepings and washings in water softened by a mixture of that already used on other goods and by working on the beam. This acts as a partial substitute for puering with dung, which is no longer used on calf-kid. Probably an oropon or pancreol bate is now employed. The goods are next drenched in the ordinary way,

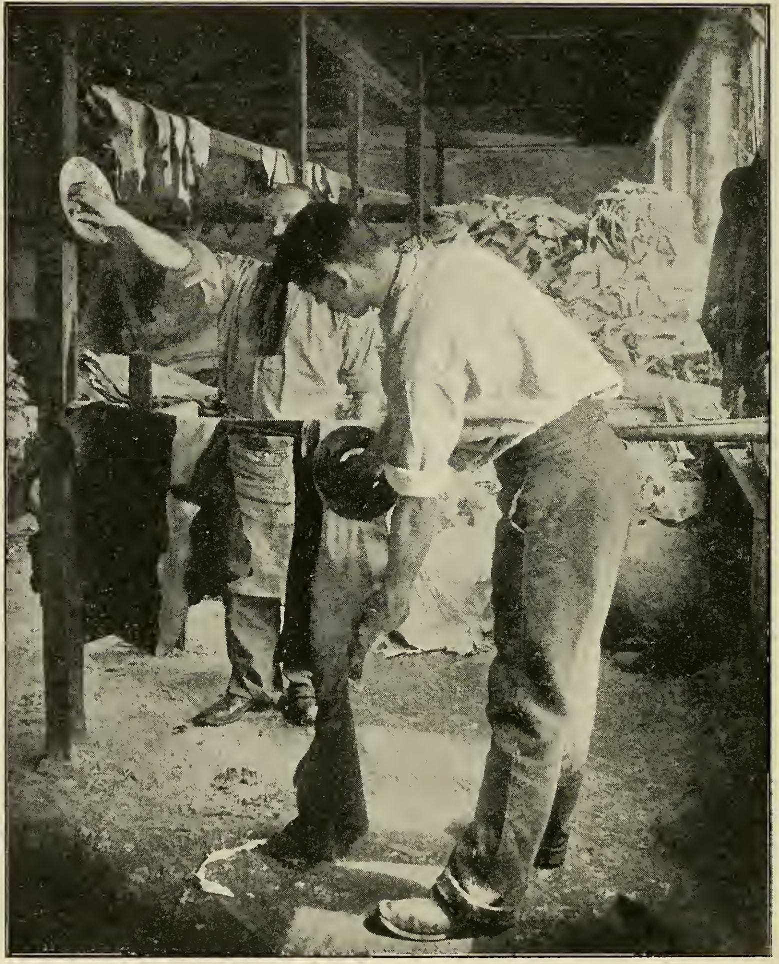

FIG. 45.—Grounding with the Moon-knife.

3 to 4 per cent. of bran being used, and the goods allowed to rise two or three times in the drench, which should be conducted with the usual precautions (p. 215) to avoid the danger of false fermentation in hot weather. The goods should come out of the drench free from lime and unswollen by acid, but full, white, and soft. The tanning (or "tawing" as it is usually called in the case of alumed goods) is done in a rotating drum with a mixture of alum or sulphate of alumina, salt, flour, egg-yolk, and olive oil. About 5 per cent. of flour, 2 5 per cent. of alum, 1 per cent. of salt, the yolks of 25 eggs or 1½ lb. of preserved egg-yolk, 2 oz. of olive oil, and 1¼ to 1½ gallon (12 to 15 lb.) of water are required per 100 lb. of wet pelt. The flour is first made into a smooth paste with a little water, the egg-yolk, somewhat diluted with warm water and strained, is mixed in together with the oil, and finally the alum and salt solution is added at such a temperature as to bring the whole mixture to blood-heat (38° C.). The length of drumming depends on the thickness of the skins, several hours being required for very thick ones, but care must be taken to stop and ventilate the drum at frequent intervals, so as to prevent the skins becoming hot by friction. This part of the process was formerly accomplished by treading with bare feet in a tub. After tawing the goods are allowed to lie in piles overnight, or are sometimes laid in tanks for a day or so with any that remains of the tawing paste, to complete the absorption of the salt and alum, and are then frequently split with the band-knife machine, though it would be better, as is often done on the Continent, to split them before tawing, the materials of which are not only costly, but unfit the splits for many purposes for which they might be employed. The drying should be rapid, but is best done first at a moderate temperature, or in the open air, and then in a rather hot stove. They may now be allowed to "age" from one to three months, but it is usually better before ageing to do the first part of the finishing process, consisting of damping back, staking, and, if necessary, shaving. Machines are now almost invariably used for the staking, the principle of which may be described as that of a pair of tongs, carrying one or generally two staking blades on one limb, and a roller on the other which closes on the skin, and presses it against and between the blades, while the tongs are drawn backwards, allowing it to slip through. Fig. 46 illustrates the Slocomb, one of the most popular machines of this type. After staking and ageing the skin is soaked in water till thoroughly wet in all parts. This not only softens it and prepares it for dyeing, but takes out the superfluous alum and salt, and at the same time a good deal

of flour and egg. To replace these "re-egging" is necessary, and while some manufacturers give egg-yolk, or egg-yolk and flour only, many add a proportion of salt, and sometimes also of alum. This is done before dyeing if the skins are to be blacked on the table, but as tray-dyeing (see p. 499) would again wash out

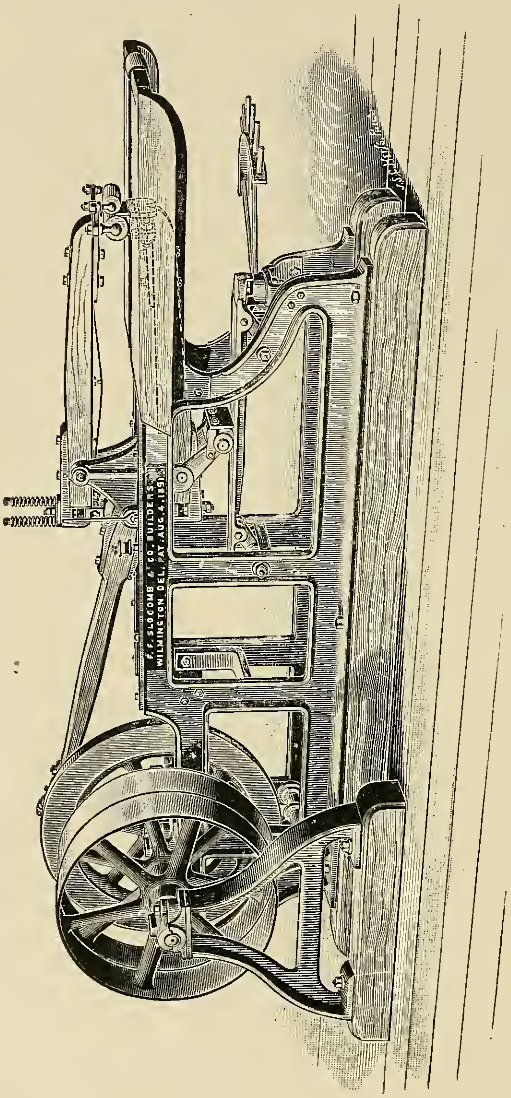

FIG. 46.—The Slocomb Staking Machine.

the egg, the re-egging is deferred till after dyeing if this process is resorted to. Before dyeing the skins receive an alkaline mordant to overcome greasiness and enable them better to take the colour. In former times this was usually stale urine, but this has mostly been superseded by solutions of "hydroleine" (a washing powder), or of soap rendered more or less alkaline with ammonia. Eitner gives the following recipe, viz. ½ lb. Marseilles (olive oil) soap dissolved in boiling water, 5 or 6 egg-yolks added, and the whole made up to 4 gallons with water and ¼ lb. potash bichromate. The colour used is infusion of logwood or its extract, or two-thirds logwood and one-third fustic,[1] which is best extracted without alkali, a small quantity of soda or ammonia being afterwards added. Coal-tar dyes are often added. It is fixed and darkened by a wash of iron-liquor or a solution of 1 of ferrous sulphate in 75 of cold water. After being again dried the skins are sometimes grounded with the moon-knife, softened again by staking or perching, for which a machine with inclined or spiral blades attached to a drum and working on a sort of leather apron is often preferred to machines of the Slocomb type, and rubbed over on the grain with a composition containing oil, wax, etc., and are finally ironed with a heavy flat iron to give them a fine and smooth surface. Eitner gives a recipe for the gloss: 1 kilo. gum arabic, ½ kilo. yellow wax, ½ kilo. beef-tallow, ¾ kilo. Marseilles soap, 1 litre strong logwood infusion, and 5 litres water. The water is brought to a boil in an earthen pot, and then the soap, wax, gum, and tallow are added successively, each being stirred till dissolved before adding the next, and lastly the logwood. After boiling for an hour it is allowed to completely cool, being incessantly stirred during the whole process. After ironing the goods are rubbed over with a final gloss, for which Eitner gives the following recipe: 8 litres olive oil, 500 grm. tallow, 500 grm. yellow wax, 500 grm. rosin, 500 grm. gum arabic (previously softened in water). The mixture is cooked for two hours in an earthen pot till the water is evaporated, and allowed to cool with constant stirring. The skins are then rubbed with a flannel with a very small sprinkling of French chalk, and are ready for sale.

The manufacture of calf-kid has been almost entirely superseded by that of box-calf, from the superior water-resisting powers of the latter, and also on account of the costly nature of the materials employed, one Leeds manufacturer in former times using not less than 50 tons of egg-yolk annually, but the leather made a very smart and comfortable boot, and a chrome calf-kid

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[1] The addition of fustic is to correct the blue-black of the logwood.

might very probably come into fashion again. The difficulties in its manufacture are, however, considerable, as it is almost impossible with basic chrome liquors to get the absolute smoothness of grain required, and for this cause chrome leathers have usually a boarded grain. It is possible that if the tawing were commenced with an alum tawing paste, and a suitable basic chrome liquor only added when the paste were almost absorbed, this difficulty might be overcome. Earlier substitutes for egg-yolk were unsuccessful, either because unsatisfactory in effect or equally costly with the genuine article, but with our largely increased knowledge of emulsions this difficulty might probably be overcome, perhaps by the use of sulphonated oils. The flour, of which the gluten only, and not the starch, is absorbed, and the proteids of the egg-yolk, which are important as fillings, might probably be replaced by other colloids of an organic nature, or by minerals such as colloidal silica or alumina phosphate.

The manufacture of glove-kid is quite similar in principle to that just described, but varied in detail to suit the softer and more delicate skins employed, to give greater softness, and especially the quality of stretching in any direction without springing back, which is so characteristic of the leather. Lamb-skins are the principal raw material, though genuine kid is also employed for the best qualities. The manufacture varies much with the quality and character of the goods. The skins, which are mostly dry, are soaked in clean and cool water for three to four days, according to age and thickness. Common qualities (small imported slink lambs) are often unhaired by dipping in or painting with a paste of gas-lime, lime and sulphide of sodium, or lime and red arsenic, so as to destroy the wool. Better skins are sometimes unhaired by painting on the flesh with lime alone or in mixture, and in other cases ordinary lime-pits are used with limes, which are most usually strengthened with red arsenic, which is added to the lime while hot from slaking (*cp.* p. 189).

The calcic sulphydrate (and perhaps sulpharsenite) thus formed hastens the unhairing, and preserves the gloss of the grain. Well conducted glove-kid establishments avoid as much as possible the use of old limes, which produce a loose, porous leather, with a rough, dull grain. The liming lasts on the average ten days, and is of the greatest importance. It is essential that the inter-fibrillary substance should be dissolved, that the leather may have the quality known in Germany as *Stand,* that is to say, may be strongly stretched in either length or breadth without springing back. It also depends upon the liming (and this is of special importance in the case of lamb-skins) whether the tissue of the fat-glands is well loosened, so that the fat, either as such, or as lime- or ammonia-soap, may be readily and completely worked out. Skins in which this is neglected can never be properly dyed.

When the hair (or wool) is well loosened, the skins are rinsed in water, and then unhaired on the beam with a blunt knife. The water employed in washing should not be much colder than the limes, or it will prevent the hair from coming away readily. The wool or hair is washed and dried for sale. The skins are thrown into water,, to which a little lime-liquor has been added, to prevent precipitation of the lime in the skins by the free carbonic acid of the water, which would have the effect of making them rough-grained.

Next comes the first fleshing (*Vergleichen*) or "levelling." By this the loose cellular tissue on the flesh side is removed, together with the head, ears, and shanks; and the flanks are trimmed. The skins are then again thrown into water softened with lime-liquor as above described, and then into a puer of dogs'-dung. This is prepared by stirring up white and fermented dogs'-dung with hot water, and straining it through a sieve or wicker basket. The puer must be used tepid, and not too strong. The skins "fall" (lose their plumpness) in it rapidly, and become extremely soft and fine to the touch; and the fat-glands, remaining hairs, and other dirt can now be very readily scudded out. One main object of the puering is to remove the elastic fibres, which are very abundant in the grain layer, and prevent stretching.

Too strong puers, or too long continuance in them, produce evident putrefactive effects on the skins (see also p. 231).

When the skins come out of the puer they are stretched and worked on the flesh with a sharp knife, and any remaining subcutaneous tissue is removed. This constitutes the second fleshing. They are then rinsed in warm water, and beaten with clubs in a tub, or worked in a tumbler-drum, in either case with a very little water only; and are finally brought into a tank of water, not too cold, and kept in constant motion with a paddle-wheel.

The skins are next cleansed on the grain side by working on the beam with plates of vulcanite set in wooden handles, so as to remove fat, lime- and ammonia-soaps, and other lime compounds, together with all remaining hair or wool. The skins are now a second time washed in the "paddle-tumbler," first in cold and then in tepid water; and after allowing the water to drain from them, they are transferred to the bran-drench.

This is prepared by soaking wheaten bran in water at about 50° C., and diluting with warm water. Sometimes the mixture is strained and the bran-water only used, to save the trouble and cost of removing adhering particles of bran from the delicate skins. Sufficient of the liquid must be employed to well cover the skins, and the temperature may range from 50° F. (10° C.) to 68° F. (20° C.). These conditions are favourable to bacterial activity, which comes into play, and, on the one hand, evolves acetic and lactic acids, which dissolve any remaining traces of lime, and, on the other, loosens and differentiates the hide tissue, so as to fit it to absorb the tawing solution. Much care is required in the management of the bran-drench, especially in summer, since the lactic readily passes into some other fermentation (see also p. 215). The tawing mixture is composed (like that employed in the manufacture of calf-kid, *q.v.*) of alum, salt, flour and egg-yolks, in a quite thin paste. A small quantity of olive oil is also generally used. The skins are either trodden in it with the feet, or more generally put into a tumbler-drum with it. Kathreiner pointed out, many years ago,[1] that a mixture of olive oil and glycerine might be partially substituted for the egg-yolks in both the tanning and dyeing of glove-kid leather.

The tawed skins are now dried by hanging on poles, grain inwards. Rapid drying in well-ventilated, but only moderately heated, rooms is essential to the manufacture of a satisfactory product.

The dry leather is rapidly passed through tepid water, and after being hung for a very short time, to allow the water to drain off, is trodden tightly into chests, and allowed to remain in them for about twelve hours, so that the moisture may be uniformly distributed. It is then trodden on hurdles (German *Horden*) composed of square bars of wood, joined corner to corner, so as to make a floor of sharply angular ridges. The next operation is stretching with the " moon-knife " ; after which the leather is dried nearly completely, and staked again.

This completes the tawing process. The goods are now " aged " as in calf-kid manufacture. Before dyeing they are washed with tepid water to remove part of the tawing mixture and, especially, superfluous alum and salt, and are re-egged much like calf-kid, before dyeing if the latter is done by brushing, and after if in the dye-tray or paddle. Aniline colours are more used than formerly, especially for topping and brightening the natural colours, but the dyewoods and other mordant colours are still largely employed. The leather is first prepared with an alkaline mordant (stale urine, ammonia, etc.) (*cp.* p. 493), then repeatedly brushed with or dipped in the dyewood liquor,

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[1] Gerber, i. (1875) p. 170 ; ii. (1876) p. 664.

and a mordant wash (" striker," German *Ueberstrich*) containing some metallic salt is generally applied, with the object either of bringing out the special tone required, or of making the colour more lively and permanent. The striker is usually a solution of one of the so-called " vitriols " : " white vitriol " (zinc sulphate), " blue vitriol " (copper sulphate), " green vitriol " (iron sulphate), a tin solution (" spirit "), or occasionally other salts.

After the dyeing the skins, if dipped, are wrung out and re-egged ; if brush-dyed, sleeked out with a brass or ebonite sleeker to get rid of superfluous water. They are then dried in an airy room. Before staking (stretching) the skins are laid or hung in a damp cellar or in moist sawdust. They are staked twice : once damp, and once nearly dry ; and are finished by glassing or ironing.

Skins which are much damaged on the grain, or otherwise faulty, are smoothed with lump pumice on the flesh side, or fluffed with fine emery on the fluffing wheel. They are then dyed on the flesh side, mostly by dipping, but occasionally with the brush, in which case the method described is slightly modified.

Tawing with alum and salt is frequently employed for commoner and stronger leathers, such as aprons (of sheep-skin), leather for whip-lashes, laces for belts, and " skivers " for capping druggists' bottles. The process is practically the same as for calf-kid, except that no egg and little flour is used. Often flour is entirely omitted, and the goods may then be alumed in tubs, in which they are merely handled, as the alum solution penetrates quickly. Goods which are required white are frequently handled or tumbled with a milk of " whitening," both to improve the colour and to neutralise any acid present, and fix the alum by rendering it more basic. Alumed goods can be stuffed with greases, either by hand or in the drum, after thorough softening by staking.

Alum and other salts of alumina are frequently used in combination-tanning with vegetable materials (see Chapter XXII.). " Green " leather for laces, " dongola," and " dog-skin " glove-leathers are made in this way. Glazed kid for ladies' shoes must be slightly vegetable-tanned on the surface or it will not glaze, but this is frequently accomplished by the use of materials in the dye-liquor containing tannins. This was long considered a French secret.

CHAPTER XVII

CHROME AND IRON TANNAGES

Both chromium and iron, like aluminium, form trivalent salts which have strong tanning properties, but in most other respects they are very different not only from it, but from each other. While the atomic weight of aluminium is only 27, those of chromium and iron are 52 and 56 respectively—nearly double as much. While aluminium, so far as is known, only forms one oxide, Al_2O_3, iron and chromium form quite a series, chromium being the more oxidisable of the two, and while alumina is amphoteric, forming not only salts with acids but aluminates with bases, the chrome and iron oxides are either acid or basic, but not both.[1] The salts of Cr'' (chromous salts) are blue, but so avid of oxygen that they can hardly be preserved, while the ferrous salts are green, and only moderately oxidisable. The trivalent salts of chromium are green or violet, while those of iron (ferric salts) are yellow or orange, and are stable in absence of reducing substances.[2] While iron has a very unstable higher oxide, forming red ferrate salts, the corresponding oxide of hexavalent Cr, chromic anhydride, CrO_3, is deep orange or red, and forms very stable chromates and bichromates, and there is yet another oxide, probably perchromic acid, which, when chromic acid is oxidised with hydrogen peroxide, can be shaken out with ether as a bright blue solution. Both ferric salts and chromates are reduced by light in presence of organic matter, but not salts of Cr_2O_3. These differences are important in many ways with regard to their tanning properties.

Metallic chromium is a grey, and very infusible, metal, derived principally from chrome iron ore, a mineral which contains the oxides both of chromium and iron. This is furnaced with a mixture of lime and soda or potash, when it absorbs oxygen from the air, the chromium becoming converted into chromic acid, which combines with the alkali present, while the iron remains undissolved as ferric oxide. On lixiviating the mass and

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[1] Sodium and potassium hydrates dissolve small quantities of chromium hydroxide to pink or green solutions, perhaps of sodium chromite.

[2] A curious exception in colour are the iron oxalates, of which the ferrous is orange-brown, while the ferric is deep green.

evaporating the solution, lime and potassium or sodium chromates are obtained, according to the alkali used, and on adding sufficient sulphuric acid to combine with half the base, potassium or sodium dichromate (or, as it is commonly called, " bichromate ") can be crystallised out. Potassium dichromate is most commonly made, because it crystallises well and is not deliquescent, but sodium dichromate is somewhat cheaper, though less convenient in storage. In making concentrated basic liquors (p. 267) its greater solubility is useful. Dichromates, at least in the crystallised state, are not hydric salts like bisulphates, but anhydrochromates corresponding to the potassium anhydrosulphate obtained by fusing ordinary bisulphate, and to fuming sulphuric acid. Thus the formula of potassium dichromate is :

$$\left\{\begin{array}{l} CrO_2OK \\ O \\ CrO_2OK \end{array}\right., \text{ or } Cr_2K_2O_7,$$

and its molecular weight is 294, while that of sodium dichromate, which is similar in constitution, but crystallises with 2Aq, is 298. The molecular weight of CrO_3 is 100. By the addition of an equivalent of alkali to dichromates, yellow normal chromates, as, *e.g.*, K_2CrO_4, are formed. Chromic acid and acidified potassium dichromate are powerful oxidising agents, and are used as such in many processes, and especially in the manufacture of alizarine. If sulphuric acid be used in molecular proportions, the product of the reaction is chrome-alum : $4H_2SO_4+Cr_2K_2O_7=3O+4OH_2+K_2Cr_2(SO_4)_4$. This, like ordinary alum, crystallises with 24Aq, and hence has a molecular weight of 998. It forms dark purple, almost black, crystals, which are a fine garnet-red by transmitted light. In cold water it dissolves to a violet solution, which becomes green on boiling, but very slowly resumes the violet condition when cold. This change, which is not uncommon in chrome solutions, is probably due to a partial decomposition into free acid and a basic salt, the basic salts of chromium being generally green. It has been noticed that raw pelt swells much more in the green than in the violet solution, and the violet solutions tan more rapidly.[1] Being derived from waste products, chrome-alum is often a cheap and valuable source of chromium for chrome tanning.

For the analysis of chrome compounds see *L.I.L.B.*, pp. 141 *et seq.*, and *L.C.P.B.*, p. 120.

Chrome is not only of importance in tanning, but in dyeing, on account of its power of forming insoluble colour-lakes with

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[1] Burton and Hey, *J.S.L.T.C.*, **4,** 1920, 205, 272.

many mordant colouring matters. For this purpose normal or basic chromic salts are sometimes used, sometimes chromic acid or dichromates, the latter acting not only by yielding chrome-oxide on reduction, but as oxidising agents to the colouring matters. Most of the colours produced with chrome mordants are of dark shades, that with logwood being deep violet or black. The mordanting power of chromium is important in the dyeing of chrome leather. Bichromate of potash is often used in dilute solution for darkening the shade of leather dyed with other materials, but is not to be recommended on account of its destructive action on the leather.

Numerous patents have been taken for processes of chrome tannage. The first practical method was described by Professor Knapp in 1858 (see p. 264), though he did not recognise its value. Some of the patents have a historical interest, though no practical importance. Among these may be mentioned that of Cavallin, a Swedish apothecary, whose object was dyeing rather than tanning, but who treated raw hide with a solution of bichromate, which was afterwards reduced on the fibre by one of ferrous sulphate.[1] The leather produced is dark reddish-brown, and tender from the amount of basic ferric salt formed at the same time. Mr J. W. Swan, well known in connection with photographic processes and electric lighting, also patented a process of chrome tannage (as an addendum to a patent on carbon printing), in which the chromic acid first fixed in the pelt was reduced by "oxalic, or other suitable acid." Although it is possible to produce leather within the lines of the patent, the strongly acid reaction of the reducing agent renders it unsuitable for practical use. The first chrome-tanning process which made any show of practical success was that patented in 1879 by Heinzerling, which was acquired in this country by the Eglinton Tanning Company, and also worked under their license for a short time by the Yorkshire Tanning Company at Leeds. Though the process was not commercially successful on any considerable scale, it possesses points of interest which make a brief description desirable. The hides or skins, after preparation in the usual way, were treated in a mixed solution of salt, alum (or aluminium sulphate), and potassium bichromate, but no systematic attempt was made to reduce the chromic acid to a tanning form, the product being, at first at least, merely an alum tannage, coloured, and perhaps somewhat hardened with chromic acid, though on

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[1] Both Chadwick in America (U.S.A. Pat. 561044, 1896) and Gottschalk (Fr. Pat. 258228) seem to have re-patented the Cavallin process with slight modifications.

keeping for a length of time reduction gradually took place at the expense of the hide-fibre and of the fats employed in currying, so that the leather internally became greyish-green, and really chrome tanned. Specimens of the early products of the process, preserved in the museum of the Leather Industries Department at Leeds, have now all undergone this change, but are still tough and flexible, showing that the rapid tendering of the Heinzerling leather, which was one of the causes of its failure, must have been due to some error in manufacture, and was not inherent in the process. Interesting, historically, is the fact that at an early stage in the life of the patent a specimen of the leather was submitted to the late Professor Hummel in order that he should suggest some means of overcoming the disagreeable yellow colour of the product. He reduced it with a bisulphite, and coloured it with an aniline dye, and a piece is still in the possession of Leeds University, and in perfectly sound condition. If legal publication of this experiment could have been proved it would have invalidated the important Schultz patents, under which most of the chrome-kid of the United States was manufactured. As bearing on modern chrome tanning, the most important reaction in the process is that of the alum with the bichromate. It has been shown by Heal and Procter[1] that pelt absorbs practically no chromic acid from bichromate unless it has been previously set free by acidification. When, however, alum or sulphate of alumina is added, its sulphuric acid liberates the chromic acid, leaving a basic alumina salt in solution, and this fact has been utilised in some modern tanning processes.

The first really important advance in practical chrome tanning was made by Augustus Schultz in 1884. Schultz was not a tanner, but a chemist employed by a New York firm of aniline-colour merchants, and his attention was accidentally drawn to leather by a friend who asked him if it were possible to produce a leather for covering corset steels which would not rust them as ordinary alumed leathers do. The process which he adopted was probably suggested by a method then recently patented for the mordanting of wool by chrome oxide, and depended on the power of the pelt to absorb free chromic acid (as it does all other free acids), and the subsequent reduction of the latter on the fibre to a basic chrome salt, which produced the tannage. The reducing substance employed was the free sulphurous or thiosulphuric acid of an acidified solution of sodium thiosulphate (hyposulphite), and as it was not certain which of the two acids was the really active agent, Schultz duplicated his patent so as

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[1] *Journ. Soc. Chem. Ind.*, 1895, p. 251.

to cover both. Though he made no claim in his patent to having discovered the best proportions of his ingredients, those which he specified have proved practically useful after allowing for the modifications required by different skins and slightly different methods of working. His first bath consisted of a solution of 5 per cent. of bichromate of potash and 2½ per cent. of concentrated hydrochloric acid (or 1 25 per cent. of concentrated sulphuric acid), reckoned on the wet weight of the prepared pelt, and dissolved in sufficient water for convenient use in the paddle or drum which was to be used in the process. In this bath the skins were worked till they took a uniform yellow colour throughout, but without any tanning effect being produced. They were now freed from superfluous chrome liquor by draining or "putting out," and transferred to the second bath, which consisted of 10 per cent. of "hypo" and 5 per cent. of hydrochloric acid similarly dissolved. In this they rapidly took a duck-egg green colour from the reduction of the chromic acid; and when this was uniform throughout the skin, the tannage was complete. The exact quantity of water is not of great importance, and good results can be obtained with anything varying from 20 to 50 gallons per 100 lb. of pelt (200 to 500 per cent.) if time be allowed for the weaker solution to act. The quantities of "hypo" and hydrochloric acid given for the second bath are often somewhat insufficient, and have to be slightly increased to complete the reduction. The reaction which takes place in the first bath is represented by the following equation, in which the weights of the materials taking part in the reaction are also given below the symbols.

Potassium dichromate.		Hydrochloric acid.		Potassium chloride.		Chromic acid.		Water.
$K_2Cr_2O_7$	+	$2HCl$	=	$2KCl$	+	$2CrO_3$	+	OH_2
294	+	73	=	149	+	200	+	18

As ordinary concentrated hydrochloric acid does not contain more than about 30 per cent. of actual HCl,[1] about 2·5 parts would be required to completely decompose 2·94 parts of dichromate, while in Schultz's formula only 2·5 parts of hydrochloric acid are used to 5 parts of dichromate, thus leaving a considerable part of the dichromate undecomposed. This excess has been found useful in the production of a good leather, both to prevent accidents from an overdose of hydrochloric acid, and

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[1] Acid of sp. gr. 1·16 (32° Tw.) contains 31·5 per cent. of HCl by weight or 36·6 grm. per litre, and therefore is practically 10 × normal strength. Acid of sp. gr. 1·2 (40° Tw.) contains 39·1 per cent., or 469 grm. per litre.

because of the modifying effect of an excess of neutral salt on the action of the chromic acid, but is not essential.

The reactions which take place in the second bath are somewhat complicated. Eitner, in a valuable series of articles on chrome tannage, which appeared in the "Gerber" during 1900, states that even better results are obtained by using the hydrochloric acid in slight excess in the first bath, as the action of chromic acid (in the presence of the potassium chloride of the chrome-bath) is not swelling but hardening to the skin, and the slight swelling action of the hydrochloric acid tends to counteract this, and also to facilitate the subsequent reduction. The two views are not contradictory, as the excess of bichromate behaves to the hide as an alkaline salt, which also produces a slight swelling effect, and it is quite probable that better results are attained when the solution is either alkaline or acid than when the potassium chromate is exactly decomposed. Eitner recommends the use of 4 parts by weight of bichromate and 4 parts of the strongest hydrochloric acid dissolved in 400 parts of water for each 100 parts of wet pelt, which should yield about 40 parts of dry leather. He states that if such a bath be used, it may be safely and economically exhausted by a second pack of skins, which is impossible in a bath containing excess of unacidified bichromate. He gives[1] the following explanation of the successive changes which take place when acid is gradually added during the reduction, but points out that in practice the reactions always to some extent go on simultaneously.

In the first stage of reduction very slight acidification is required, and if the skins have been chromed with excess of hydrochloric acid, may be altogether dispensed with. The skins become brownish from the conversion of the chromic acid into so-called "chromium dioxide" (probably really a basic chromic chromate, $Cr_2CrO_4(OH)_4$, which on ignition leaves Cr_3O_6); no sulphurous acid is liberated or sulphur deposited, but sodium tetrathionate is formed in the bath, and the reaction may be represented as follows :—

$$(1)\quad 3CrO_3+6HCl+6Na_2S_2O_3=3Na_2S_4O_6+6NaCl+3OH_2+Cr_3O_6.$$

Further addition of hydrochloric acid brightens the colour of the skins, while the liquid still remains clear, and chromium chloride is formed instead of chromic chromate, the main reaction being :

$$(2)\quad 2CrO_3+12HCl+6Na_2S_2O_3=3Na_2S_4O_6+2CrCl_3 \\ +6NaCl+6OH_2.$$

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[1] Gerber, 1900, p. 297. See also Stiasny and Das, *J.S.C.I.*, 1912, p. 753.

On still further addition of hydrochloric acid, sulphur is separated according to the following equation, and is deposited partly in the skins and partly in the bath :

(3) $2CrO_3+6HCl+3Na_2S_2O_3=3Na_2SO_4+3S+2CrCl_3+3OH_2$.

After complete reduction and consumption of the free hydrochloric acid, further reactions take place at the expense of the excess of thiosulphate which should be present, resulting in the production of basic chromic salts, and the further deposition of sulphur, mostly within the skin, as shown in the following equations :

(4) $Cr_2(SO_4)_3+Na_2S_2O_3+OH_2=2CrOH.SO_4+SO_2+S+Na_2SO_4$.

(5) $2CrCl_3+Na_2S_2O_3+OH_2=2CrOH.Cl_2+SO_2+S+2NaCl$. [1]

The thiosulphate bath, therefore, not only reduces but precipitates sulphur in the skin, and reduces the chromic salt to a basic state. In boiling solution thiosulphate precipitates the whole of the chromium as chromic oxide, but in the cold, and in presence of free sulphurous acid, it only reduces to a basic salt. Eitner does not consider the possibility, which certainly requires investigation, that instead of basic salts, sulphite-sulphates are formed, at least in the first instance. Such salts of one base and two acids are quite possible, and it is known that the presence of acids even as weak as carbonic allows much more alkali to be added without causing precipitation.

The free sulphur which is liberated is partially deposited on and among the fibres of the leather, and adds to its softness, and also acts chemically on the oils used in " fat-liquoring," so that it is probably one of the main causes of difference between the products of the Schultz or " two-bath " method and the " one-bath " processes subsequently to be described.

It does not fall within the scope of this book to describe in detail the working methods for the production of the different kinds of chrome leather, but a few precautions common to all forms of the process may be named. It is not absolutely important in all cases that goods should be completely freed from lime before chrome tannage, but in this case a sufficiency of acid must be allowed in the first bath to neutralise the lime introduced. Fairly thorough liming is generally advisable to plump and

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[1] Obviously the proportion of these reactions will vary with the concentration of the solutions and the rate at which acid is added. Stiasny states that more tetrathionate is formed if even a trace of arsenic is present in the acid used.

separate the fibres, but as a rule the bating or puering of goods for chroming should not be excessive,[1] but should be planned not to remove more than is absolutely necessary of the hide-substance, as the chrome tannage is in its nature soft and light, and does not lend itself to artificial fillings, such as the flour and egg-yolk of the calf-kid process. Skins are sometimes freed from lime by "pickling" (p. 238), and pickled skins may be chromed without depickling, as the acid will be removed by the dichromate, but in this case the acid contained in the skins must be considered in the composition of the chroming bath. Skins, indeed, which are pickled with a sufficiency of acid may be chromed in a neutral dichromate bath, and this is sometimes a convenient mode of procedure. To prevent drawing of the grain during tanning, skins not unfrequently receive a preliminary tannage with alum or sulphate of alumina, and these materials, together with salt, may be introduced into the chroming bath, in which case they will liberate a portion of the chromic acid, as has been mentioned in connection with the Heinzerling process. Alum, chrome-alum, and acid salts, such as sodium bisulphate, may be substituted for the acid in the chrome bath, but organic acids must not be used, as they would reduce the chromic acid. The quantity of free chromic acid in the chrome bath is of the most vital importance to success, as it, and not the dichromate (which may be present in considerable excess), regulates the amount of chrome taken up by the skin and the subsequent degree of tannage. It is very possible to injure leather by over-chroming, rendering it rough, harsh, and even tender. If a bath containing excess of bichromate is to be re-strengthened, it may be assumed as a rule that all the free chromic acid has been absorbed by the skins, and while it is merely necessary to restore the strength of the dichromate to its original amount, the full quantity of acid must be used which would be required in preparing a new bath. Where, as in Eitner's acid chrome bath (p. 259), the whole of the chromic acid is liberated, the bath may be exhausted by a second pack of skins. Many tanners, in order to avoid complications of remaking a bath, run away their chrome liquors

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[1] Goat-skins for glacé kid need thorough puering to produce a smooth grain. It has recently been shown that one considerable result of puering is to remove the layer of elastic fibres which are specially abundant in the grain of goat-skin, and prevent the flattening out of the grain-surface which is required in glazed goat (see p. 223). In some experiments made by Mr Wilson, twenty-four hours in a pancreatic bate were necessary for their complete solution, but a shorter time would probably be practically sufficient. It has been usual in the States to puer as much as sixteen hours with dog-dung.

after once using, and containing all the excess of dichromate which has been used. With proper chemical control this is not necessary, and is objectionable, not only from its wastefulness, but on account of the very poisonous character of the unreduced bichromate. Even weak dichromate solutions, especially if warm, are liable to cause painful and obstinate eruptions on the hands, but this rarely occurs to tanners, as the poisonous action of the solution is removed or much lessened on reduction. It is well, therefore, to arrange that men who handle skins in the chrome bath should subsequently also work in the reducing bath, and to avoid, as far as possible, contact of chrome liquors with the skin. Methods of analysis of used chrome liquors are given in *L.I.L.B.*, pp. 142 *et seq.*; *L.C.P.B.*, p. 120. Those for the determination of acidity are not however easily applicable in the presence of alum and salts of chromic oxide.

The skins on coming from the chroming bath may be allowed to lie for some time without serious injury, but should be carefully protected from the action of light, which reduces the chrome at the expense of the skin, and renders the subsequent tannage irregular. It is found that skins, if brought into a weak or neutral reducing bath, are apt to " bleed " or lose chromic acid, which is reduced wastefully in the bath. On the other hand a strong " hypo " bath is apt to draw the grain and contract the skins, owing to the tannage taking place too suddenly. A somewhat strong " hypo " bath is therefore often employed as a preparatory " dip," the skins being simply drawn through it to fix the chrome on the surface, piled on a " horse," and subsequently reduced in a bath of ordinary strength. The tendency to bleed is lessened, but at the expense of the pelt, by the reduction which takes place if the skins are allowed to lie overnight in the chromed state. Eitner states that skins chromed in an acid bath (*i.e.* where the whole of the chromic acid is in a free state) show little tendency to bleed, and it is probable that the bleeding is mainly of undecomposed dichromate. After reduction the skins are well washed with warm water, and their later treatment is the same as that of skins tanned by the one-bath process, which is subsequently described (see p. 264).

Naturally in practical work the reduction cannot be made to proceed rigidly in the definite steps described by Eitner on p. 259, but all go on in different proportions together, though by supplying the acid in proper quantities and at proper intervals, they may be made in the main to follow in the given order. Both on this account, and because neither the exact amount of chromic acid in the skins, nor the sulphurous acid lost by escape into the air can be determined, the reduction cannot be conducted on theoretical principles, but the best conditions must be empirically determined. Eitner states that 12 parts of thiosulphate dissolved in 400 parts of water and 6 parts of (40 per cent.) hydrochloric acid are sufficient for 4 parts of bichromate per 100 of wet pelt employed in the chrome bath, of which not more than one-half to two-thirds is absorbed ; and that if equal parts of bichromate and acid are employed in chroming (4 parts of bichromate to 10 parts of commercial strong acid), the acid used in reducing may be lessened to 5 parts. In this case it must not be forgotten that if the partially exhausted chrome bath is used for a second pack of skins, which are afterwards finished in a bath of full strength, nearly the whole quantity of bichromate used in making up one bath will be absorbed by the skins. The amount of acid consumed in reduction will be greater the more rapidly it is added, owing to increased escape of sulphurous acid. It is better to add the acid, previously diluted with water, in eight or ten successive portions, more rapidly at first and more slowly during the latter half of the operation, each portion of acid being added as soon as no further change of colour appears to be caused by that already given. These changes are the more rapid the lighter the goods. The colour darkens at first to olive-brown, then gradually becomes green, and finally blue, and when this colour is uniform throughout the thickness of the goods, no further acid need be added. For goods which have been chromed in an acid bath, Eitner states that no acid will be needed for the first twenty to thirty minutes. It is important to have a sufficient excess of thiosulphate in the bath when reduction is complete, in which case the goods may be left for some hours or overnight in the bath to complete "neutralisation," but Eitner prefers to use a fresh bath of 1½ parts of thiosulphate in 400 parts of water for this purpose, the bath being used, after settling, for making up the reduction bath for the next lot of goods, for which 1½ parts less thiosulphate is used. The goods must be kept in motion during reduction, either in a drum or a covered paddle.

Eitner describes a method of working the two-bath process which is very economical both in material and labour, and which ought to be quite successful on many classes of goods.[1] The prepared pelts, delimed or bated, are placed in a drum with a pickle of 10 lb. of salt and 1 lb. of sulphuric acid in 10 gallons of water per 100 lb. of wet pelt, and are run one or two hours according to thickness. A solution of 3 lb. of bichromate is now added to the pickle in the drum, and run two hours more, or

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[1] Jettmar, *Handbuch der Chromgerbung*, 2nd edition, p. 358.

until the pelt is evenly chromed and yellow throughout. A solution of 15 lb. of thiosulphate ("hypo") in 10 gallons of water is now added to the liquor in the drum, and 5 lb. of diluted hydrochloric acid is gradually run in in small portions. The leather will first become brown from the deposition of chromium chromate, but as more acid is added will take the regular clear blue-green. The solution left in the drum should not be more than tinged with green. The goods should be well washed, but "neutralisation" is probably not absolutely necessary unless the goods are to be fat-liquored.

As soon as the Schultz process proved successful many attempts were made to evade the patent by the use of other reducing agents than the "hypo" and other salts of sulphurous acid which it covered, and almost every imaginable reducing agent was patented. Among these the use of hydrogen sulphide and acidified solutions of alkaline sulphides, and especially of polysulphides,[1] proved capable of practical use, though less convenient than thiosulphate, but were soon acquired by a combination, the Patent Tanning Company, together with Schultz's original patents.

Under these circumstances Martin Dennis, either by fresh discovery or otherwise, revived the original process of Knapp (p. 256), which he patented[2] almost in Knapp's words, and offered a basic chrome tanning liquor for sale, without further restrictions on its use. This liquor was made by dissolving precipitated and washed chromic hydrate (easily prepared by precipitating chrome-alum solution with excess of alkali) in hydrochloric acid to saturation, and adding washing soda until the solution was rendered sufficiently basic. Such a solution may be used on skins prepared in the ordinary way by diluting with water and strengthened as the tannage proceeds, like a vegetable tan-liquor. It is doubtful if the patent was a valid one, as it was known that the use of such a solution was not new, and it was only granted in America on the representation, which has since been found to be mistaken, that chlorides alone were applicable for tanning, while Knapp had not restricted his statement to these salts. In reality chlorides and sulphates seem equally suitable, but to produce similar results the former must be made more basic than the latter. In any case the patent could not cover the general principle of basic tanning, but only the particular liquor and

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[1] "Liver of sulphur" or solutions, made by boiling sodium sulphide or soda with excess of sulphur.

[2] Martin Dennis, U.S.A. Pat. 495028, 1893; and 511411, 1893, 7732, 1893. Eng. Pat. Gallagher.

mode of preparation specified. It was soon afterwards shown by the writer[1] that a good chrome tanning liquor might be prepared by direct reduction of dichromate with sugar or other carbohydrates in presence of such a limited quantity of hydrochloric acid as to produce a basic salt. Suitable proportions are 5 mol. HCl to 1 mol. potassium dichromate, which produces a salt approximately $Cr_2Cl_3(OH)_3$. The solution is easily made by dissolving 3 parts of dichromate of potash or soda in a convenient quantity of water, adding 6 parts by weight of concentrated hydrochloric acid, and then cane-sugar or glucose gradually till a green solution is obtained, when the whole may be made up to 100 parts, and will be approximately of the same strength as a 10 per cent. solution of chrome-alum. A little heat may be needed to start the reaction, but too much should be avoided, as considerable heat is evolved by the oxidation; and as much carbonic anhydride is produced, which causes the solution to effervesce briskly, the vessel used should be of ample size. In place of cane-sugar a good quality of glucose may be used, but some samples contain some impurity which produces a violet solution which will not tan satisfactorily, though it may be made to do so by sufficient addition of alkali. This liquor is in regular use in many tanneries, producing a good quality of chrome calf, but is somewhat variable in its effects according to the temperature employed in its preparation, and it appears to have no real advantage over a simple solution of chrome-alum rendered basic by soda. A somewhat similar preparation is Eberle's "chromalin,"[2] in which some organic substance, probably crude glycerine, is used to reduce the bichromate. The organic matters, and especially the organic acids which result from the oxidation of the sugar or glycerine, are not without influence on the tanning properties of the liquor. Of course these solutions may be rendered still more basic by the addition of sodium carbonate. A good stock-liquor, of approximately the same strength as that above described, is made by dissolving 10 parts of chrome-alum in 80 parts of tepid, but not hot, water,[3] and adding with constant stirring a solution of 2½ to

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[1] *Leather Trades Review*, Jan. 12, 1897.

[2] Compare Eberle's German Patents 119042, 1898, and 130678, 1899. The last of these appears to be anticipated, at least as regards the use of glucose, sugar, and starch, by the writer's publication in 1897, above cited.

[3] Later investigations have shown that the temperature of the water is unimportant if alkali be added, but chrome-alum dissociates to some extent in hot water, and comparative experiments have shown that solutions of the normal salt made with the aid of heat act on skin as if more acid than those made in the cold.

3½ parts of washing soda in 10 parts of water. The chrome-alum dissolves somewhat slowly without the aid of heat, and the solution is best made either in a small drum driven by power, or by suspending the crystals in a basket near the surface of the liquor, so that the saturated solution can descend.

Eitner [1] has pointed out the important effect that differences of basicity have on the tanning properties of chrome solutions. Normal chrome sulphate or chrome-alum colours the leather quickly and equally throughout, and swells the pelt on account of its practically acid character, but gives a thin and lightly tanned leather, from which much of the chrome washes out, unless it is at once " neutralised " in alkaline solutions. As the chrome solution is made more basic the tannage penetrates more slowly, but is heavier and more thorough, the colour is darker and bluer, and much less of the chromic salt is removed by washing with water. When the basicity becomes excessive the solution becomes unstable, and decomposes on dilution with water or on contact with the skin into a very basic salt which is precipitated, and a more acid solution than that given by a moderately basic salt. The effect of such solutions on the leather is very unsatisfactory, producing the bad effects both of too acid and too basic salts. The pelt is apt to be swollen and lightly coloured by the more acid salt, but at the same time the actual tannage proceeds very slowly, and in extreme cases it is difficult to tan through, while the surface becomes over-tanned and discoloured. and the grain often tender and even brittle from the incrustation of precipitated basic salt. Eitner likens the effect of the more acid liquors to the quickly penetrating and lightly tanning vegetable tans, such as gambier, and that of the more basic to the heavier tannages, such as valonia ; and within limits, advantage may be taken of these facts in adjusting the liquors to the character of the leather it is desired to produce. In sulphate liquors, he considers the salt $CrOH . SO_4$ as most suited to general use, and in the case of chrome-alum this is produced by the use of 286 parts of soda-crystals, or 106 parts of dry sodium carbonate (1 molecule) to 998 (or practically 1000) parts by weight (1 molecule) of chrome-alum. (In using washing soda, care must be taken to employ *clear* crystals of the salt, and not those which have become white by loss of water, or to allow for the greater strength.) In place of soda Eitner makes a similar basic liquor by boiling 1000 parts of chrome-alum with 248 parts (1 molecule) of sodium hyposulphite until the whole of the liberated sulphurous acid is driven off and the sulphur deposited. In comparative experiments by the

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[1] Gerber, 1901, pp. 3 *et seq.*

Author no difference could be detected between the tanning effects of the two solutions, and that with soda is both cheaper and more easily made. If the solution with hyposulphite is not boiled a more acid liquor results, in which part of the chromium is probably combined with sulphurous acid, forming an unstable compound which may prove useful in certain cases. Borax, sodium sulphite, and many other weakly alkaline salts may also be used.

Since the war the use of bichromates as oxidants in the dye industry has apparently diminished, and, in any case, chrome-alum has been not merely dearer, but more difficult to obtain ; and this has led to a larger production of chrome liquors from bichromates, and especially from sodium bichromate. In his Cobb lectures to the Society of Arts[1] the writer published a method of making a concentrated chrome tanning solution by the reduction of a 40 per cent. solution of sodium bichromate with gaseous SO_2, which he has since learned had been in use as a secret by one firm, and which is said to have been first suggested by Mr Balderston, the SO_2 being made by burning sulphur with air under pressure. The following equation represents the final result, though there is some doubt as to the actual course of the reaction :

$$Na_2Cr_2O_7+3SO_2+H_2O=Na_2SO_4+2Cr(OH)SO_4.$$

It will thus be seen that the solution is already basic, and can be used on many classes of leather without addition of alkali, but contains considerable excess of SO_2, which, though it possibly does not actually enter into combination with the chromium, increases the hydrion concentration, and raises the "precipitation point" (p. 270) of the liquor. Probably from this cause it tans very rapidly, and has come much into use.

A very similar solution might no doubt be made by the addition of Boake's metabisulphite of sodium in small successive portions to a solution of sodium bichromate of 4 lb. per gallon. The equation for the setting free of SO_2 from metabisulphite is

$$Na_2S_2O_5+H_2SO_4=Na_2SO_4+OH_2+2SO_2,$$

so that $1\frac{1}{2}$ molecules of metabisulphite and of sulphuric acid would be required to oxidise one of bichromate, and in round numbers $2\frac{1}{2}$ lb. of metabisulphite and 2 lb. of concentrated sulphuric acid for 4 lb. of sodium bichromate would be required to fulfil the equation, but in practice somewhat more, to provide for an excess of SO_2 in the liquor, and to allow for some escape of

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[1] *Journ. Roy. Soc. of Arts*, 66, 1918, pp. 747, 776.

the gas. The finished liquor should smell pretty strongly of sulphurous acid, and give a clear blue-green on dilution.

The effect of weak, and especially of volatile, acids in increasing the hydrion concentration of chrome liquors, and so lowering the precipitation point, and rendering possible the use of solutions extremely basic as regards their fixed acid, deserves more attention than it has hitherto received. Burton has shown [1] that even carbonic acid has a noticeable effect of this sort.

Excellent chrome liquors are also made under the patent of J. R. Blockey,[2] in which the suitably acidified bichromate is reduced by spent tanning material, which is added in excess, that which is not oxidised and dissolved being left in the vat for use on the next batch, so that no residue remains to be removed.

Eitner stated that he had made chrome solutions of various types, containing organic compounds in combination with the chrome salt, which combine with the leather, producing a fuller and softer tannage, but he gave no details as to their preparation, as they were made commercially by the " Erste Oesterreichische Soda-Fabrik " at Hruschau. The writer has found that in some cases by the addition of, say, three parts of sugar, or still better of glucose, to ten parts of the chrome-alum in making up the basic liquor, a much fuller and plumper leather is produced, which dries perfectly soft, even without staking or fat-liquoring ; and it is probable that many other organic compounds may be found which produce similar effects. The addition of very small quantities of neutral tartrates or lactates, or of any other hydroxy-salts or acids, have, however, a remarkable effect in lowering the apparent basicity of the solution and preventing tannage. This is due to the property of hydroxy-acids of forming complex ions with chromium, which do not tan, and it has been shown by Procter and Wilson [3] that solutions of Rochelle salt (sodium potassium tartrate) will dissolve all but traces of chrome from chrome leather, and leave it in a condition in which it can be boiled for glue-making. The Rochelle salt acts best for this purpose in a neutral or alkaline condition, and may mostly be recovered by suitable acidification, when it is precipitated as the very sparingly soluble potassium tartrate, and may again be brought into solution by the addition of soda. It is highly probable that the unsatisfactory tanning liquors produced by direct reduction with some samples of glucose are due to the presence of small quantities of some such organic acid produced during the oxidation. It has

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[1] Burton, *J.S.L.T.C.*, 4, 1920, 205 ; Burton and Hey, *ibid.*, 272.

[2] Blockey, Eng. Pat. 131772 ; *J.S.C.I.*, 1919, 783 A.

[3] Procter and Wilson, *J.S.C.I.*, 1916, p. 156.

been found that these solutions may be made to tan by the liberal addition of soda. It is probable that more satisfactory results in chrome tanning will be attained by the direct addition of known organic substances to basic liquors of definite constitution than by the somewhat uncertain products of organic oxidations.

The quantity of salt to be added depends on the qualities desired in the leather, and upon whether chloride or sulphate liquors are employed ; salt in chloride liquors increasing the softness of the leather, but in excess tending to flatness, while in sulphate liquors it practically diminishes their basicity by converting the chromium sulphate into the equivalent chloride, which, as Eitner points out, behaves as a less basic salt, and hence but little advantage is to be gained from its use. It is best to begin with a very weak liquor to avoid drawn grain, and for the same purpose a preparatory tannage with alumina salts, or an addition of alum or sulphate of alumina and salt, may be made to the first liquor, as the attraction of the chrome salt for the fibre is sufficient to produce a chrome tannage, even in presence of excess of alumina salts. Ten lb. of chrome-alum will tan about 100 lb. of wet pelt, but more must be used for the first parcel ; to avoid loss of time, the skins may be tanned out in a pretty strong liquor. The bath has a tendency to become acid by use, and before strengthening it may be necessary to add some more soda solution. Little, if any, additional salt is required, as it is only absorbed by the skins to a small extent, probably as chromic chloride. As the liquors gradually become charged with sulphates, it is best to work them out like bark liquors, and not to go on strengthening the same liquor indefinitely. If old liquors are used for green goods, it is not necessary to neutralise them with soda before use, as Eitner has shown that less basic liquors colour more evenly and with less tendency to produce drawn grain.

The cause of this increase of acidity in the liquors is that the basic chrome salts hydrolyse on dilution, and that the acid diffuses much more rapidly than the basic chrome, so that at first the liquor must be kept acid to prevent the precipitation of the basic salt ; but as the process proceeds the hide becomes saturated with acid, which is not further absorbed, while the fixation of the chrome salt still continues, and the excess of acid tends to prevent a full tannage. It is therefore necessary to maintain the basicity of the final liquors, either by strengthening with very basic solutions or by the addition of alkalies. This is controlled by determining the chrome by oxidation (*L.I.L.B.* and *L.C.P.B.*, p. 122) and titration with potassium iodide, and subsequently titrating the acid with caustic soda in a boiling solution, and calculating the "basicity number." This number is the proportion of sulphuric acid to the atom (52) of Cr. For the normal salt it is therefore 144, and diminishes as the basicity increases, the practical values ranging about 96, corresponding to $SO_4Cr(OH)$. It was suggested by Stiasny when working on chrome sulphates, and of course was quite appropriate for his purpose, but is less convenient when working with chlorides or other salts. A much better way would be simply to give the proportion of (OH) to Cr_2 (104). In this case the value of chrome hydrate $Cr_2(OH)_6$ would be 6, with less values for less basic solutions. It is preferable to adopt Cr_2 rather than Cr, as it gives a larger scale of whole numbers, and fits better with sulphates, while chrome chloride is very frequently written Cr_2Cl_6.[1] A practical way for the tanner of determining the basicity of liquors is that of McCandlish's "precipitation point," which has a more direct relation to the tanning properties of a liquor than the exact acid determination, which varies in its effect with different acids. The chrome liquor is filtered perfectly clear with the addition of a little kaolin, and 10 c.c. is titrated with constant stirring with a N/10 or N/20 solution of sodium carbonate, or of whatever alkali (*e.g.* borax) is used for neutralisation, until a permanent turbidity is produced which does not disappear on stirring or shaking. This gives the largest quantity of alkali which could be added. How much the tanner should stop short of this in practice is a question of experience, but a higher margin must be left with green goods than with hides nearly tanned. In the early stages the absorption of acid by the skin is frequently so large that a portion of the basic chrome salt is precipitated and the liquor becomes turbid.

Chrome sole leather has become of some importance, and when well manufactured it is probably the most durable and waterproof leather known for the purpose, though it is to be feared that all supplied during the war did not merit this character. It is usually tanned by suspension in the ordinary basic chrome liquors, and should at least be well washed and neutralised slightly, perhaps with thiosulphate, dried to a sammed condition and rolled or struck out, and then thoroughly dried (often nailed on boards for the sake of flatness) at a rather high temperature,

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[1] It has been proposed in America to express the "acidity" of chrome liquors in an analogous but inverse way. Cr_2Cl_6 and $Cr_2(SO_4)_3$ have an "acidity" $=6$, $Cr(OH)Cl_2$ and $Cr(OH)SO_4=4$, $Cr(OH)_2Cl$ and $Cr_2(OH)_4SO_4 =2$, whilst the acidity of $Cr_2(OH)_6$ is zero. The number here is that of the monovalent acid radicals combined with 2Cr.

and impregnated by suspension in a bath of melted waxes, and hung over the hot tank to drain thoroughly, when, after cooling, it is ready for use.

A method of tannage which gave excellent results on a small scale was as follows :—The butts, after rounding, but without deliming, were placed in a 10 per cent. solution of alumina sulphate till well penetrated and slightly swollen, and were then treated with a pretty strong basic liquor, made by reduction of sodium bichromate with sulphurous acid, in which they tanned very rapidly. The leather was of a light and even colour, and decidedly thicker than test-pieces tanned in basic liquors in the usual way after deliming. Both liquors could be used repeatedly.

The best waxing mixture is somewhat a secret, and mixtures with too much paraffin wax slip badly in wet weather. The writer has had good results from a mixture of two parts of pale rosin and one of paraffin wax, with a little tallow to soften it slightly.

Basic chrome liquors, such as have been described, may also be used in chrome combination tannage. It is generally best to let the light vegetable tannage precede the chrome, and lightly tanned skins, such as "Persians" and East India kips, acquire many of the qualities of chrome tanned leather by the treatment. The effect is still further increased by a previous detannisation of the leather with alkaline solutions (see p. 379). Many firms now supply basic chrome liquors ready prepared for use.

The time required for chrome tannage will of course vary with the thickness of the goods, and for calf-skins will usually extend over some days, though it can be much quickened by drumming. The tannage is generally best accomplished in the paddle, but can be carried out by frequent handling in pits or tubs, or, where very smooth grain is important, by suspension. When the goods come out of the final liquor they may be allowed to lie in pile for twenty-four hours, or even for some days, with advantage, as the surplus chrome liquor is pressed out, and the tannage becomes more complete. They are then washed with plenty of warm water, till it ceases to be coloured with chrome. They may be kept for an almost unlimited time in a wet condition, as they do not bleed, and have little tendency to heat even in pile. They have now reached the stage at which we left the "two-bath" leather, and the subsequent treatment may be the same in both cases.

Although by both processes the chrome salt fixed in the fibre is of a decidedly basic character, it still contains enough acid to act injuriously on the leather in course of time, and to lead to serious inconveniences in its subsequent treatment. Before proceeding further this excess of acid must be removed or neutralised, and it is not too much to say that most of the troubles experienced in fat-liquoring arise from neglect or mistake in the washing and neutralisation. The difficulty in the process arises from the fact that while the acid should be reduced to a mere trace it must not be entirely removed,[1] as chromic oxide itself does not seem capable of tanning, and at any rate the effect of excess of strong alkalies is at once to render the leather hard and pelty. Borax is one of the safest neutralising materials, about 3 per cent. on the wet weight of the pelt being required in not more than $\frac{1}{2}$ per cent. solution. Eitner recommends the use of silicate of soda, which, sold as a solution of sp. gr. 1·5, is somewhat stronger and much cheaper than borax. Hyposulphite of soda and whitening together neutralise more rapidly and completely than either alone. Other salts of weak acids may also be used, the acids exercising a regulating influence which prevents neutralisation going too far. Sodium carbonate or bicarbonate, or ammonia, may also be used, but with these it is difficult to get even "neutralisation," or to avoid the risk of carrying the process too far. Stiasny's mixture[2] of 2 per cent. of soda crystals and 2 per cent. of ammonium chloride or sulphate, to which 2 per cent. more soda and 1 per cent. more ammonium salt may be added if the neutralisation is not sufficient, is perfectly safe and efficient, and cannot over-neutralise, and statements about its expense are unfounded, since the mixture can be used repeatedly, merely strengthening with soda and a little ammonium salt as required, since it is really the soda which neutralises, and the ammonia acts only as a "buffer" to regulate the hydroxyl concentration. Even a thorough drumming with a milk of "whitening" (calcium carbonate) or magnesia is effective. With the latter there is no danger of overdoing the process, but in some cases the adhering whitening and precipitated calcium sulphate are troublesome in later operations. In any case the neutralising should only be carried so far that the skins show no acid reaction to litmus paper ; and whatever means of neutralising are employed, the fat-liquoring should take place without delay, before the more acid liquor in the centre of the skin has time to diffuse again to the surface.

It is probable that one of the great causes of difference between "one-bath" and "two-bath" leathers is the presence of free sulphur in the latter. This may also be introduced into "one-

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[1] Procter and Griffith, *Journ. Soc. Chem. Ind.*, 1900, p. 223.

[2] *Colleg.*, 11, 1912, p. 293.

bath " leather, by treating it in the wet chromed state, without washing out the chrome liquor, with excess of a solution of hyposulphite, or of an alkaline polysulphide, which at the same time will neutralise the skin. The more acid the chrome liquor, the greater the quantity of sulphur which will be introduced. The simplest means of distinguishing " two-bath " from " one-bath " tannages is to test for the presence of sulphur, by wrapping up a silver coin with a piece of the leather in paper, and leaving the parcel for an hour in the water-oven, or some other warm place, when the presence of sulphur will be shown by the blackening of the coin. Of course a sulphurised " one-bath " leather will give the same reaction.

The leather must now be dyed and fat-liquored. Which of these two operations should be first undertaken will depend on circumstances. Most leathers dye more easily before fat-liquoring, but if acid dyes which are soluble in the alkaline fat-liquor are used, a good deal of colour is often lost. This may be compensated by dissolving a suitable aniline (acid) colour in the fat-liquor. " Bluebacking " is generally done before fat-liquoring by drumming with methyl violet or some other aniline colour (with or without logwood, which gives alone a very dark violet). Any shaving or splitting required must of course be done before bluebacking.

The fat-liquor is an emulsion of soap and oil, which for chrome leather should be as neutral as possible if the neutralising has been thorough ; but if any acid be left on the skins, a neutral fat-liquor will be precipitated as a greasy mass. This can sometimes be remedied by the addition of a little ammonia or borax, or by re-fat-liquoring with soap solution only, but if the washing of the skins has been incomplete, and soluble chrome salts remain, the mischief is almost irretrievable, as sticky chrome-soaps are formed, often coloured with the aniline violet, which adhere to the skins, and which can scarcely be removed by any solvent which does not injure the leather. As regards the soaps and oils used, there is considerable latitude : 1½ per cent. of castor-oil soap and ¾ per cent. of castor or olive oil on the wet weight of the pelt has done good service in my hands, but many manufacturers employ soft soaps, curd soaps, etc., with castor, olive, cod or neatsfoot oil, and sometimes sod-oil or degras. Eitner considers olive oil and olive oil potash soap the most suitable, and particularly warns against the use either of drying oils or of oils containing tallow (such as neatsfoot), which are not only apt to cause a white efflorescence, but to give the leather a disagreeable rancid smell. Fish oils are unsuitable, but mineral oils are often useful constituents of fat-liquors. Wool-fat also makes a good fat-liquor, but is unsuitable for goods which are to be glazed. "Turkey-red oil" (which is sulphated castor) may be used as a fat-liquor, simply mixed with warm water without soap, and has been recommended where delicate colours are to be dyed after fat-liquoring; but it is said to have an unsatisfactory after-effect, hardening and tendering the leather.[1] Some soaps made from the saponifiable part of wool-grease, such as "Lanosoap," also act well in conjunction with olive, castor, or other oils. Where leather is to be glazed, the amount of fat-liquoring must be kept very moderate. Fat-liquors should be thoroughly emulsified, and are generally used warm. They penetrate better if the leather is partially dried by sleeking out, or pressing, or cautious "samming," but the leather must not be completely dried out before fat-liquoring and dyeing, unless it has been previously treated with glycerine, glucose, treacle, or some deliquescent salt, which will enable it to be wet back. Chrome leathers are not "waterproof," as has often been stated, unless rendered so by treatment with soaps and greases, and are apparently easily wetted, but the fibre will no longer absorb water after thorough drying, and consequently will neither dye nor stuff satisfactorily. In order to enable chrome leather to be kept in an undyed condition glycerine or syrup is sometimes mixed with the fat-liquor, but as the watery portion of this is not generally completely absorbed, the process is somewhat wasteful. Mr M. C. Lamb avoids this difficulty by applying a solution of glycerine to the grain side with a sponge after fat-liquoring. In this case the leather may be dried sufficiently for staking or shaving without risk.

Chrome leather can be dyed by many of the acid aniline colours without a mordant. Basic colours are only fixed when the leather has been first prepared with a vegetable tannin, gambier or a mixture of gambier and sumach being the most suitable. Considerable care must be employed in the application of tannins to chrome leather, as they have a tendency to harden it and diminish its stretch, or even to render it tender, but traces of tannin in the dye probably facilitate glazing. Before dyeing

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[1] This is somewhat doubtful if the oils are satisfactorily prepared and free from excess of acid, and in any case sulphonated oils, not merely castor but other vegetable oils, have come largely into use, and as such fat-liquors are not to any great extent alkaline, and may even be acid, they do not strip dyes, and are not so readily precipitated if the neutralisation is not quite complete. Sulphonated fish-oils are largely used in other branches of the trade and have great emulsifying powers, but the writer has no experience of their use on chrome leather.

it is advantageous to fix the tannin with tartar emetic, or, for browns and yellows, with titanium potassium oxalate solution, which itself gives a good yellow-brown with tannin. In place of employing the tannin and titanium salt in two separate baths they may be combined, using a weight of the gambier or tanning extract (oakwood, chestnut, etc.) about equal to that of the titanium salt, or titanium tanno-oxalate solution may be used. Chrome leather may be dyed with the various dye-woods, which are mordanted by the chromium present, but the colours are mostly dull, that of logwood being nearly black. A good black of a very permanent character is obtained by dyeing with logwood, and saddening with a hot solution of titanium oxalate in the drum. Iron-logwood blacks are much used on chrome leather, often in conjunction with coal-tar dyes, and a little iron-alum added to the chrome liquor in tanning will facilitate dyeing the skins black with logwood and help it to penetrate through the leather, which is sometimes desired. Several aniline blacks give very satisfactory blacks by brushing or dyeing. For suitable dyes consult App. C.

Chrome skins may be glazed in the ordinary way with blood or albumen mixtures under glass or agate, but require good pressure and repeated seasonings and glazings, and much care is required in fat-liquoring. The glazing is often assisted by the previous application of barberry juice (*épine vinette*) or of lactic or tartaric acid solution with a trace of sugar. Much of the difficulty which has been experienced in glazing chrome leathers is due either to the natural fat of the skin, or to oils used in fat-liquoring in excessive quantity or of unsuitable character.

Iron tannages may be very shortly dismissed, as their practical interest is at present mostly either historical or prospective ; and the salts of iron have been discussed in connection with those of chrome. It is well, however, here to insist again on their action as oxygen carriers, which is often very destructive, especially on vegetable tanned leather. Ferric salts in contact with more easily oxidisable matters readily give up oxygen, and pass into the ferrous state ; and especially does this happen in the presence of organic matter under the influence of sunlight. Thus iron-salts often act as carriers of oxygen, and oxidisers of organic matter, absorbing oxygen from the air, and giving it up again under the influence of light or heat to any organic matter with which they are in contact. Thus when used in dyeing black, it is important that there should be considerable excess of tannin or of colouring matter present. There is also little doubt that the presence of ferric salts in leather blacks has a great tendency to cause the resinification of the oil, known as "spueing," by promoting its oxidation.

The ferric salts are characterised by giving blue-black or green-black compounds with tannins and with many other allied bodies, while the corresponding ferrous compounds are mostly colourless, though they rapidly oxidise and darken on exposure.

Ferric iron, like alumina, forms an "alum," a double sulphate of iron and potassium, $Fe_2(SO_4)_3K_2SO_4,24Aq$, forming fine pale violet crystals, but dissolving to a yellow-brown solution. (It must be distinctly understood that iron-alum and chrome-alum contain no alumina, but are simply called alums because of their similarity of constitution, iron or chrome taking the place of the aluminium. Iron-alum, in conjunction with salt, can be used for tanning, giving a pale buff-coloured leather very similar to an ordinary alum leather. Thus the presence of a small quantity of iron in an alum used for tawing is of no consequence, except as affecting the colour of the leather. In impure sulphate of alumina, such as "alumino-ferric," it, however, generally exists in the green ferrous state, and only acquires tanning properties on oxidation. Without common salt iron-salts are still less satisfactory tanning agents than those of alumina under the same conditions, as the acid is yet more loosely held, and though basic ferric salts are taken up in considerable quantities by hide, the leather produced is thin, and usually brittle. Professor Knapp devoted much study to the production of a commercial sole leather by basic iron-salts, and took several patents, which did not prove practically successful, though the brittleness was to some extent overcome by the incorporation of compounds of iron with organic materials such as blood and urine, of iron-soaps, and of rosin and paraffin in the leather. Like most mineral tannages, the process was far more rapid than that with vegetable materials. Knapp's basic tanning liquor was made by the oxidation of ferrous sulphate with a small quantity of nitric acid. Patents have been taken for the oxidation of ferrous sulphate by peroxide of manganese in presence of sulphuric acid, which produces basic ferric sulphate in mixture with manganese sulphate, which has also some tanning properties. Attempts have also been made to tan by treatment of the hide with solutions of ferrous sulphate and subsequent exposure to the air, in order to oxidise the iron on the fibre and convert it into a basic ferric salt, but have not proved of any commercial value.

Owing to the scarcity of tanning materials in Germany during the war and the great demand for leather, considerable attention was paid to iron-tanning, and quite a number of patents were taken out, and some of them claim to be successful in producing merchantable leather. Dr J. Bystron [1] treats first with ferrous sulphate, and oxidises on the fibre with ferric nitrate. The "Chemischen Fabriken," Worms, patent the use of ferric formates; [2] Moos and Kutsis [3] of Stuttgart, the use of iron-salts in conjunction with sulphite-cellulose liquors; and Dr Otto Röhm has taken a variety of patents [4] for iron tannages in conjunction with aldehydes and other things. The great difficulty appears to be to produce a leather which will not become brittle on keeping. More hopeful are the numerous patents which have been taken for combinations of chrome and iron tannages, and there is no doubt that a merchantable leather can be made on these lines. For details and a good general review of iron tanning processes the reader may be referred to Ing. Josef Jettmar's little book *Die Eisengerbung*, published by Schulze and Co., Leipzig, 1920. No attention appears to have been paid to combined iron and aluminium tannage, which would seem worth experiment, as the combined salts would be very cheap, most natural clays containing both metals, and their properties being in some ways complementary. It is said that iron tannages cannot be neutralised with alkalies without destruction.

[1] D.R.P. 255324, 1910.

[2] Aust. Pat. 80067, 1918.

[3] Swiss Pat. 81781, 1918.

[4] Swiss Pat. 74849, 1916; 75618, 1916; Aust. Pat. 77867, 1919.

CHAPTER XVIII

VEGETABLE TANNING MATERIALS

As has been stated in the previous chapter, our knowledge of the chemistry of tannins is not sufficiently advanced to render possible any strictly chemical classification, while an additional complication arises from the fact that very different tannins may coexist in the wood, bark, fruit, galls, etc., of the same plant. It therefore seems best to follow the example of Professor Bernardin in his *Classification de* 350 *matières tannantes,*[1] and arrange the plants under the orders of the natural system of botany, as has already been done by von Höhnel[2] and A. de Lof,[3] and considerable use has been made, not only of these books, but of the recent exhaustive work of Dekker[4] on the vegetable tanning materials, and of the various lists which have from time to time appeared in the scientific press. In the following pages only those materials which from their high percentage of tannin, or from some other cause, seem of commercial interest or value are included, as the tannins are so widely distributed in the vegetable kingdom that any exhaustive list would be quite out of the question.

Tannins are not confined to any particular part of the plant, though they are usually most abundant in barks and fruits. Insect-galls are often very rich in tannin, usually gallotannic acid; while in several cases woods are of commercial importance from their cheapness, though the percentage of tannin they contain is not generally high. The function of tannins in the vegetable economy is not well understood. In some cases they are probably a waste product of plant-life, and may help to ward off attacks of insects. They usually exist as cell-contents, and as vegetable cells have frequently thick and impermeable walls, and the diffusive power of tannins is low, much time is required for extraction, unless the cells have been previously crushed or broken.

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[1] Gand, 1880.

[2] *Die Gerberinden*, Berlin, 1880.

[3] *Matières tannantes*, Halle aux Cuirs, Paris, 1890. See also *Agricultura Ledger*, 1902, No. 1 (Government Printing Office, Calcutta, 6d.), by Mr. D. Hooper, which contains much valuable information, and various Indian Forestry Reports.

[4] Dekker, *Die Gerbstoffe*, Berlin, 1913.

It would be beyond the scope of this text-book to describe in detail the structures of the tannin-yielding parts of plants; but barks are of such general importance, that some particulars seem desirable.

The detailed structure of bark varies greatly in different trees, though its general principles remain unaltered. One of the best short accounts of these is given by Professor H. Marshall Ward on page 199 of his little book on *Timber and Some of its Diseases*,[1] and further information may be found in Van Tieghem's *Traité de Botanique* and other works on structural botany.

With regard to detailed structure of various tanning barks, *Die Gerberinden* of von Höhnel[2] is one of the best authorities.

The inner surface of the bark of a young tree, or twig, consists of a layer of soft and living cells resting on the outer surface of the wood, called the *cambium*. These cells multiply by division (*cp*. p. 11), and produce from their inner surface the successive annual layers of wood, and on their outer a fibrous tissue called the bast (*phloem*), consisting of lengthened cells, and tubes with perforated divisions (sieve-tubes) which convey sap, and mostly run in the direction of the branch, but are crossed transversely by cells in a line with the medullary rays of the wood. All these cells when first produced in the cambium-layer have thin and soft cellulose walls, but the inner layer forming the wood becomes lignified, or hardened, by deposits of lignine on the interior of the cell-walls, while their contents of living protoplasm disappear. The outer layer forming bast remains much softer and more fibrous, and retains its vitality longer. The outer surface of the young branch is covered by a thin layer of flat cork-like cells forming the epidermis, developed from the growing tissue of the bud, beneath which is a layer of growing cells frequently called the *cork-cambium*. This produces, on its inner side, a layer of soft, juicy, thin-walled cells (*parenchym*), which are living and capable of growth, and contain protoplasm and often chlorophyll, to which the green colour of young twigs is due. This layer at first rests on the bast. On the outer side, the cork-cambium produces corky layers beneath the epidermis. The section of an oak-twig is shown in fig. 47.

As the tree grows, it is obvious that the corky epidermis which grows in thickness, but not in breadth, must become distended and finally ruptured. In some cases the surface is renewed by fresh corky layers constantly developed below it, and then the bark remains smooth and unfurrowed, as in the beech and young oak, or in the birch, from which thin corky layers are continually

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[1] Macmillan & Co.

[2] *Die Gerberinden*, Berlin, 1880.

peeling; or it may produce a thick layer of cork, as in the cork-oak. In many cases, and especially in older trees, the outer or primary layer of cork-cambium ultimately dies for want of nourishment, and a fresh cork-producing layer is developed in the still living parenchym. As cork is practically air- and water-proof, the new layer cuts off from its source of nourishment and kills all the parenchym exterior to it. In some cases this peels off, as in the Oriental plane (*Platanus*), but usually it forms a constantly increasing coat of dead tissue forming the "ross" or "crap" (Ger. *Borke*), which, as it cannot increase in breadth, becomes deeply fissured as the tree becomes old. In some cases the new growing layer or secondary cork-cambium forms a complete coating parallel with the first, but more often it consists of a series of arcs convex towards the tree and cutting the primary cork-cambium at various places, so as to divide the tissue outside itself into scales. Later on the process repeats itself, new arcs forming inside the first, and cutting off further portions of the parenchym.[1] In this way the cork-forming layer gradually sinks deeper and deeper into the bark, till it frequently

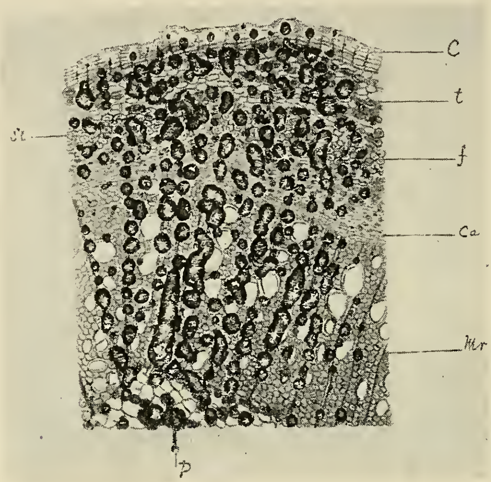

FIG. 47.—Section of Oak Twig, drawn by Professor Bastin; *C*, corky layer; *t*, tannin-cells; *f* and *St*, stone-cells, etc.; *Ca*, cambium; *Mr*, medullary ray; *P*, pith.

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[1] This structure is particularly obvious in the outer bark of the hemlock and Aleppo pines.

passes even into the bast-layer, and very complicated arrangements of tissue result, in which corky layers from the secondary cork-cambium are interspersed with bast-cells and sieve-tubes.

As a rule the outer and dead part of the bark contains but little tannin, though to this there are exceptions, as, for instance, in the hemlock and Aleppo pines. It always contains a large proportion of dark colouring matters (reds, phlobaphenes, p. 342).

Cork consists of thin, and often roughly cubical, cells, which are filled with air, while tannin is usually contained in somewhat similar cells with thicker walls. The walls of many vegetable cells are perforated with fine holes, and become thickened by internal deposits of hard ligneous matter which sometimes almost fill the entire cell ("stone-cells"). Bark-cells often contain starch-granules, frequently of peculiar and characteristic forms (which are easily recognised by the blue colour produced on treating the preparation under the microscope with a drop of a solution of iodine in potassium iodide), as well as crystals of oxalate of lime and other matters. These, and the form and arrangement of the cells as seen in sections under the microscope, form useful marks of recognition of the various barks. Tannin is most easily detected by staining, before cutting sections, with a solution of ferric chloride in absolute alcohol.

Apart from microscopic characteristics, the external appearance of barks, both to the naked eye and by the aid of a lens, forms a valuable means of recognition. The arrangement of the bast and corky layers, the remains of epidermis, or the form and character of the fissures, and of the lenticels or small corky protuberances which take the place of stomata in the epidermis, should be observed.

Space does not permit of any detailed account of the structure of fruits, woods, and leaves, which are also cellular structures in many respects resembling the bark. The cuticles of leaves, and especially the stomata or breathing pores, and the hairs are often very characteristic (*cp.* figs. 59–66, and p. 309).

Valuable hints may also be obtained from the chemical reactions which are described on pp. 70 *et seq. L.I.L.B.*

Botanical List of Tanning Materials[1]

CONIFERÆ, Pines, Cypresses, mostly containing Catechol-tans, yielding reds

Abies excelsa, Lam. (*Pinus Abies, Pinus Picea, Picea vulgaris*, Link.), Norway Spruce. *Fr. Faux sapin*; Ger. *Fichte, Rottanne.* The source of the so-called larch-extract, and a principal tanning material of Austria. Contains 7 to 13 per cent. of a catechol-tannin and much fermentable sugar, and on this account is useful for swelling and colouring, but does not tan heavily. English and Scandinavian bark does not seem much utilised. Best bark 2 to 8 mm. thick; smooth, yellow inside, with reddish-brown ross outside. For detailed description of structure see von Höhnel, *Die Gerberinden*, p. 35.

Abies pectinata, Silver Fir. Fr. *Sapin*; Ger. *Edeltanne, Silbertanne, Weisstanne.* Used to a limited extent, but apt to be confused with spruce. Contains 6 to 15 per cent. iron-blueing tannin. Used in Styria, Austria, Russia. Without "ross," but silver-grey and smooth outside. (Von Höhnel, *Die Gerberinden*, p. 40; "Gerber," 1875, p. 375.)

Abies (*Pinus, Tsuga*) *canadensis*, Hemlock Fir (fig. 48).[2] The principal American tanning material, and source of hemlock extract; averages 8 to 10 per cent. of a catechol-tannin, but variable; 18 per cent. reported, possibly from a different species. Abundant in Canada and the Northern and North-western States of America. The bark of old trees, which is principally used for tanning and extract-making, is 2 to 4 cm. thick, smooth and yellow within, greyish and deeply fissured without. The ross, which is red and thick, contains a considerable quantity of tannin, with much dark-red phlobaphen. It does not differ in structure from the inner living and yellow "flesh." The bark is easily recognisable by its well-marked concave lamellæ of cork, cutting off successive layers of "ross" of several millimetres in thickness. (Von Höhnel, *Die Gerberinden*, p. 42.) (*Cp.* p. 280.)

Abies alba (*Picea alba*), White Spruce, North America. In character of tree and bark very similar to Norway spruce.

Larix europæa D.C. (*Abies* or *Pinus Larix*), Larch. Fr.

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[1] The percentage of tannin given where the source of information is not stated must in many cases be regarded as uncertain, many analyses having been made before the introduction of modern methods, but those quoted as having been done in the Author's laboratory are of recent date, and have been made by the hide-powder method.

[2] Bastin and Trimble's "American Coniferæ," *American Journal of Pharmacy*.

Mélèze; Ger. *Lärche.* Contains 9 to 10 per cent. pale catechol-tannin, mild and suitable for light leathers. Used, especially in Scotland, for basil tannage.

Pinus halepensis, Aleppo Pine. An important tanning material of the Mediterranean coasts. The outer bark, stripped like cork from the living tree (*Scorza* or *Cortegia rossa*), is a deep red tannage, and contains about 15 per cent. of tannin very similar to hemlock. It is largely used in the island of Syra. The inner and fleshy part of the bark, only obtained when the tree is cut, is *Snoubar* or *Snobar* bark, containing up to 25 per cent. of lighter coloured tannin. This bark is reddish-brown, and pretty smooth on both sides, except for shell-like depressions on the outer

FIG. 48.—Hemlock Fir (*Tsuga canadense*).

surface. The " scorza rossa " is dark red-brown internally, grey and irregular outside, frequently very thick, and divided into successive layers of 1 to 2 mm. thickness by cork lamellæ (p. 280). (Von Höhnel, *Die Gerberinden*, p. 44.) In appearance the tree resembles the Scotch fir.

Pinus tæda, America ; *P. Laricio*, Austrian Pine ; *P. maritima*, Mediterranean ; *P. Cembra*, Alps, Tyrol, 3 to 5 per cent. ; *P. sylvestris*, Scotch Fir. Ger. *Kiefer* ; Fr. *Pin sauvage*, 4 to 5 per cent. *P. longifolia* Roxb., India, 11 to 14 per cent.

Juniperus communis, Juniper. Bark used in Russia.

Podocarpus elongata and *Thunbergii*, Cape of Good Hope ; *Geelhout*, Yellow woods.

Phyllocladus trichomanoides, New Zealand ; *Tanekahi, Tarsekahi, Kiri-toa-toa*, " Golden Tan." Used in dyeing glove-leather. Tannin, 28 to 30 per cent. ; gives green-blacks with iron.

P. asplenifolia, Tasmania, Celery-topped Pine ; 23 per cent. *Phyllocladus* belongs to Yew family.

P. rhomboidalis, Tasmania, 20·6 per cent. bark (Dekker), and red colouring matter.

Callitris calcarata, Australia ; bark 21 per cent. tannin.

Most pine barks contain more or less tannin.

LILIACEÆ

Scilla maritima, Squill. Tannin stated from 2 to 24 per cent. More valuable for pharmacy.

PALMÆ

Areca catechu, Betel-nut Palm of India. Yields a species of cutch of no importance for tanning. Fruits yield an extract " Rossa," and contain 10 to 15 per cent. tannin, but no catechin.

Sabal serrulata, Saw Palmetto of Florida (Trimble). (" Dwarf " palmetto is *S. Adansonia*.) Palmetto root has been much talked of as a tanning material, and makes a light-coloured leather.

An extract has been made from the roots of the Saw Palmetto, which grows freely in the Southern States of America, and is especially abundant on the east coast of Florida. The plant is an evergreen, the stem growing flat along the ground, being held in place by numerous roots each the size of a pipe-stem. The leaves are fan-shaped and ribbed, and 2 to 3 feet in diameter. In its hardihood the palmetto resembles a weed, as the leaves may be cut off quite close to the stem without damaging the plant, which will grow freely on poor sandy land which is worthless for other purposes. The average yield is stated to be about 10 cwt. to the acre, but in good seasons and with rich land over a ton per acre has been obtained.

The air-dried leaves contain about 13 per cent. of tannin, but the results obtained by different chemists vary from 5 to 20 per cent. Possibly these variations are caused by the different amounts of moisture in the various samples. Trimble (1896) found very little tannin, and does not consider the plant of importance.

The leaves must be treated with a solution of caustic soda to remove the glossy siliceous shield which covers them and prevents their being easily extracted. After the tanning matter has been extracted the remaining fibre can be profitably disposed of to paper and rope manufacturers.

As the supply of palmetto is very large it was expected that it would, to a considerable extent, substitute the employment of gambier, and in the United States the extract met with a considerable sale, but does not seem to have been sent to England in any quantity. Samples of the extract examined by the Author analysed from 16 to 22 per cent. of tanning matter and several per cent. of mineral matter, and produced a very soft and mellow leather of good colour. The extract contains noticeable quantities of common salt, and organic salts of soda which leave sodium carbonate on ignition.

Cocos nucifera, the Cocoa-nut Palm, also contains tannin in roots.

CASUARINÆ

Casuarina equisetifolia L. (*laterifolia* Lam.); *Filao* bark, Reunion; *Tjamara laut*, Java; Casagha or Tinian Pine, Ceylon. Widely distributed in Southern Asia; bark used for tanning and dyeing. Tannin gives blue-blacks with iron. Several other species very similar in structure and properties. (Von Höhnel.) Hooper found 11 to 18 per cent. of tannin.

SALICACEÆ (Willows)

Most of the Willow tribe contain more or less iron-blueing and, presumably, pyrogallol-tannin in the bark, and many have been long used for tanning, especially in Russia. The original "suède leather" was a combination tannage of the bark of *Salix arenaria* with alum and salt, and when this process was introduced in

France the commoner *Salix capræa* was substituted, with additions of oak bark and madder to compensate its deficiency in tannin and colour. Russia leather owes part of its odour to tannage with willow bark.

Dekker gives *Salix albá* L., bark 9·4 per cent. tannin.

Salix capræa, bark 12·1 per cent. tannin.

Salix fragilis L., 9 per cent. tannin ; *S. Russeliana* (a variety), 12 per cent.

Salix repens or *arenaria* L., Astrachan, 13 per cent.

Poplars belong to the same natural order, and their bark, especially that of the Aspen (*Populus tremula* L.), has been used for tanning, but contains only about 3 per cent. tannin.

MYRICACEÆ

Myrica Gale, Sweet Gale, or bog-myrtle, contains tannin.

Myrica Comptonia or *asplenifolia*, U.S.A. ; "Sweet Fern." Covers millions of acres in Michigan. Yields 40 per cent. of "extract." Leaves 4 to 5 per cent., roots 4 to 6 per cent. tannin, according to season (Trimble). Has been much talked of, but in Professor Trimble's opinion is not likely to prove of much importance.

Myrica nagi (Hind. *Kaiphal*), India, contains 13 to 27 per cent. of tannin in the bark, and a colouring matter, myricetin, identical with that of sumach.[1] Leather tanned with it is of a somewhat reddish colour, which is much brightened by sumaching, and converted into a pale yellow by treatment with alum. It promises to be a valuable tanning material.

BETULACEÆ

Alnus glutinosa, Common Alder. Fr. *Aulne* ; Ger. *Erle.* Contains 16 to 20 per cent. iron-green tannin, with much red colouring matter ; old barks as low as 10 per cent. Colour develops during and after tannage. Used alone it gives a red, hard and brittle leather, but with galls, valonia, etc., it produces a satisfactory tannage. Its principal use is to furnish gunpowder-charcoal, and it is possible the bark might be obtained from powder-factories if the use of gunpowder is not superseded by nitro-compounds. (Von Höhnel.) The fruits have also been used in tanning. An important fuel-tree in high latitudes.

Alnus maritima, *Hannoki*, Japan ; and *A. firma*, *Minibari.*

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[1] Perkin and Hummel, *Trans. Chem. Soc.*, 1896, p. 1287.

Fruits (*yashi*) contain 25 per cent. tanning matter (iron-blueing), and little colouring matter. Used in Japan for dyeing and tanning. *A. nepalensis* and *A. nitida* used in India. Several other species of *Alnus* contain tannin.

Betula alba, White or Common Birch. Fr. *Bouleau blanc*; Ger. *Birke.* Inner bark used in Scotland (in conjunction with larch for tanning sheep-skins), Norway, Russia, etc. It contains only 2 to 5 per cent. of iron-greening tannin, and much fermentable sugar. The outer bark, "*Naeve,*" covered with turf, is used in Norway for roofing, and is very durable and quite waterproof. By far the most important use of birch bark in tanning is to produce the birch-bark tar used to give scent and insect-resisting power to "Russia" leather (*Youft*; Ger. *Juchten*). The outside bark consists of thin layers of cork, often white with a crystalline deposit of betulin, which when distilled yields the odorous oil. The distillation is a dry one, and tarry products accompany the true oil, and at first give a strong empyreumatic smell to the leather, which it loses by keeping, while the true "Russia" odour remains. This "ageing" may be hastened by hanging the leather in a hot stove. If the oil is distilled in a current of steam, or with petroleum ether, the tarry matter passes over, while the matter giving the true odour remains in the retort (p. 452).

Betula lenta, American Black Birch. The bark and twigs distilled with water yield an essential oil, which is almost pure methyl salicylate, and largely substituted for oil of wintergreen (*Gaultheria procumbens*), with which it is chemically identical. Used for perfumery, and as a rheumatism remedy. Often erroneously spoken of as the source of "Russia" oil. A mixture of a trace of wintergreen oil with sandal-wood oil considerably resembles the "Russia" scent (p. 453). Synthetic methyl salicylate is now made, but its odour, though pleasant, is different from that of the natural oil. The bark contains about 3 per cent. tannin.

CUPULIFERÆ

Castanea vesca, True or Spanish Chestnut. Fr. *Châtaignier*; Ger. *Kastanie.* Abundant in Italy, South of France, and Corsica, where it forms great forests. Bark said to be nearly as strong in tannin as oak (up to 17 per cent., de Lof, more probably 6 to 8 per cent.), but not much used in tanning.

Wood only contains 3 to 6 per cent. tannin, but is the source of the valuable chestnut extract, first employed for dyeing, and introduced as a tanning agent by Aimé Koch. The strength of extract is of course very variable, even for the same density (see Chapter XXIV.), but it usually contains from 28 to 32 per cent. of tannin. The wood is a valuable timber, and is now grown in England for this purpose, as it is much quicker in growth than oak.

The tannin gives blue-black with iron, but is not identical with either oak-bark or gall tannins, but apparently a mixture, or possibly a methylated derivative of the latter, and identical with oakwood tannin, or so nearly so as to be indistinguishable ; it may also be identical with divi tannin. Decolorised chestnut extracts sometimes mixed with quebracho and other materials are often sold as " oakwood " or " oak-bark " extracts. The extract gives a firm leather, with a good deal of bloom if used strong, and a more reddish tint than valonia. The extract often contains dark colouring matters, and the colour of leather tanned with it is readily darkened by traces of lime derived from calcareous waters or imperfectly delimed hides. Like all wood extracts it tans rapidly, the colour penetrating first, and the tan following, but, according to Eitner, it does not, alone, make full or solid tannage, perhaps from want of acid-forming matters, but answers particularly well in combination with spruce-bark. It is largely used in England for sole leather in combination with valonia, myrobalans, and other materials.

The higher the temperature of extraction, and the more colouring matter is contained in the extract in proportion to tannin matter, the greater is its viscosity. Much colouring matter remains undissolved if the extract is dissolved in cold water, but there is, in addition, a loss of tanning power, the colouring matter being also capable of combining with hide, and it has in fact been used for tanning by dissolving it in solutions of borax or alkaline salts. By improved methods of manufacture the colouring matter has been much reduced.

The chestnut is an important food tree, the nuts forming a considerable part of the food of the inhabitants of Corsica and Sardinia, and even of Italy.

Oaks

Almost all species of oak contain useful quantities of tannin in the bark, and probably in the wood. Most if not all oaks yield catechol-tannins with, probably, some mixture of ellagitannic acid.

Quercus robur, Common Oak. Fr. *Chêne*; Ger. *Eiche*. It is frequently separated into the two subspecies:—

Quercus pedunculata. Commonest oak of lowlands, England, Ireland, and Scotland. Acorns in bunches or spikes on a stalk $\frac{1}{6}$ inch long, hence Ger. name, *Stiel-Eiche*. Leaves sessile or short-stalked. In favourable situations, *said* to yield about 2 per cent. more tannin than *Q. sessiliflora*, but this is doubtful. It is the commonest oak in Slavonia, and the source of commercial oakwood extract.

Q. sessiliflora, Ger. *Traubeneiche*. Common in hilly districts, and scattered throughout the country. Acorns in bunch on the branch, or with very short stalk; leaves on stalk $\frac{1}{2}$ to 1 inch long.

Of English barks, Sussex and Hampshire are considered the best, and contain up to 12 to 14 per cent. of tanning matter; a coppice bark from Wastdale, Cumberland, is, however, recorded to have yielded 19 per cent. tanning matter (Hellon).

Probably each of the two varieties of oak gives best bark where it thrives best (von Höhnel).

Belgian bark is sometimes equal to English, and contains 10 to 12 per cent. tanning matter. Dutch bark as exported is generally inferior, and not cleaned; Swedish is bright, but very poor.

Oak-bark contains a tanning matter, quercitannic acid, giving green-blacks with iron-salts, and possibly containing both catechol and pyrogallol groups, but its constitution is not fully understood. It yields both red anhydrides and ellagic acid; and gallic acid has been obtained by the action of hydrochloric acid, though not by fermentation in the tannery. The tannin is not a glucoside, but the fact that a sugar, lævulose, is also present in the bark has led some observers to erroneous conclusions regarding the constitution of the tannin. The unpurified infusion of the bark of *Q. robur* gives a blue-black with iron-salts, from the presence of a colouring matter; but those of most other oaks give green-blacks.

Most tannin is contained in the living part of the bark. The yield diminishes in trees over twenty-five years, and coppice barks, from absence of ross, are often strong, and also contain less colouring matter and more fermentable sugar.

Warm and rich soils seem to yield the best barks.

The brighter the colour of the fresh-cut "flesh," the better the bark. Dark brown inner side shows that bark has been exposed to rain, which deteriorates strength and colour; but a very light colour is thought by some to indicate poorness in tannin. White lichen is said to be a mark of poor bark, and probably indicates a damp and unfavourable situation.

Oaks are generally cut when the sap is rising (15th April to 15th June), when the buds open and new soft cells begin to grow, for the bark is then more easily detached.

Experiments in France have shown that the bark of timber felled at other seasons may be loosened by steaming, and it is said there is no practical loss of tannin. Superheated steam, produced in a small boiler in the woods, is used.

The bark is peeled with tools of various forms, the branch and knotted places being loosened by beating with a mallet. The bark must be peeled immediately the tree has been felled.

The peeled bark, in pieces up to 3 feet long, is laid on hurdles sloped in such a way that the rain runs off as much as possible, and in this way it is dried, but in wet seasons is much damaged. Bark so dried in the woods often retains 40 to 50 per cent. water, and must be stacked or stored so as to allow of further drying.

English bark is sometimes sold in "long rind," and sometimes "hatched" or chopped in pieces about 4 inches long. Belgian and Dutch barks are generally hatched. Belgian tree bark is "cleaned" (and cleanings often mixed back with bulk), Dutch bark is not cleaned. Much sand and dirt is contained in most Continental bark: screenings of Belgian bark yielded a black liquor, and contained so much sand that they would not even burn!

Oak-bark extract is occasionally offered for sale, but is not usually genuine or of good quality, except that of the American chestnut-oak, *Q. prinus*, from which an excellent extract has been manufactured in the Alleghanies. Factitious extracts often contain myrobalans and quebracho.

Oakwood contains only a very small percentage (from 2 to 4 per cent.) of a tannin practically identical with that of chestnut, but different to that of oak-bark. It is stated by de Lof to reach 9 to 14 per cent. in old heart-wood, but this is doubtful. The wood retains the tannin in its interior for a long time. Wood of a Roman bridge built at Mainz 55 B.C. is stated by de Lof to have still contained 1·14 per cent. tannin in A.D. 1881. A good deal of imitated oakwood extract is undoubtedly made from chestnut wood, and unfortunately no very satisfactory way of distinguishing it is known, though oak-bark extract can be distinguished from oakwood by giving a precipitate at once, even in dilute solution, with bromine-water, while the wood gives a brown precipitate only after long standing. Precipitation by bromine-water is a general characteristic of catechol-tannins, and hence a mixture of quebracho (a cheap catechol-tan) with chestnut would simulate oak-bark in this respect. If a few drops of the non-tannin solution or an alcoholic extract from the "total soluble" of extracts containing quebracho or other catechol-tannins be treated with concentrated sulphuric acid in a test-tube a deep crimson will be produced, especially at the surface of the acid, which remains pink on dilution with water. With pyrogallol derivatives, such as genuine oakwood, a yellow or brown only is produced (J. Hughes). The test is very delicate. Another distinction is that bark extracts contain perceptible traces of manganese, but this cannot be relied on, as many wood extracts also contain some, probably derived from the twig and branch bark which is used along with the wood. Oakwood extract is now manufactured on an enormous scale in Slavonia, and is used both by sole and dressing leather tanners, chiefly to increase

FIG. 49.—Turkey Oak (*Quercus cerris*).

the strength of the layer liquors. The extract is also used to increase the weight of leather after tannage by mopping on the flesh side. All the best oakwood extract manufacturers contract to sell on analysis and colour estimation, and good Slavonian oakwood extract generally contains 26 to 28 per cent. of tanning matter, giving a tintometer measurement of 4° to 5° red and 20° to 25° yellow when a solution containing ½ per cent. of tanning matter is measured in a 1 cm. cell. For particulars of the manufacture of concentrated extracts see p. 493 *et seq.*

FIG. 50.—Cork Oak (*Quercus suber*).

Q. cerris, Turkey Oak. Ger. *Zerreiche.* Common in Southern Europe; a fine tree, but bark inferior to *Q. robur* (fig. 49).

Q. pubescens. Fr. *Chêne velu*; Ger. *Weiss-* or *Schwarzeiche.* In mountain districts and scattered in Southern Europe, about equal to *Q. robur.*

Q. ilex, Evergreen Oak. Fr. *Chêne vert, Chêne yeuse*; Ger.

Grüneiche, Steineiche; Span. and Ital. *Encina.* South Europe, Algeria. Said to be somewhat stronger in tannin than common oak, yielding 5 to 11 per cent. of a rather darker-coloured tannin, but well adapted to sole leather. Good bark is smooth outside, without fissures, short in fracture.

Q. suber, Cork Oak. F. *Chêne liège*; Ital. *Sughero, Suvero* (figs. 50, 51). The outer bark is cork; the interior bark contains 12 to 15 per cent. of tannin, which is redder than that of ordinary oak. Trees at first produce an irregular cork, sold as "virgin cork" for ferneries, etc. After this is stripped, later growths are more uniform, and fit for use; tanning bark is only obtained when the tree is cut down. Bark is rough but pale-coloured on both sides, and about 1 cm. thick; interior like ordinary oak, but more strongly furrowed. Produced chiefly on Mediterranean coasts, and formerly largely used in Ireland.

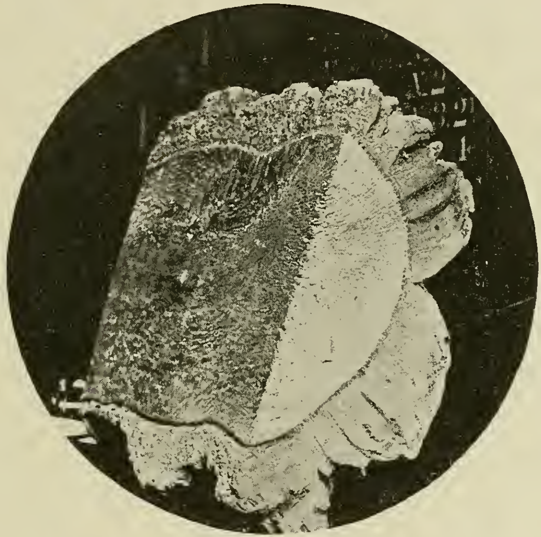

FIG. 51.—Section of Cork Oak, showing cork, inner bark and wood.

Q. pseudosuber, African Oak. Fr. *Chêne faux liège.* Algeria. Not stronger than English oak, but with more colouring matter, hence strikes quickly through leather. Bark very thick.

Q. Mirbecki. Fr. *Chêne Zeen.* Algeria. Rapid growth. Bark contains 8 per cent. of tannin.

Q. Tozæ. Fr. *Chêne tauzin.* Pyrenees and S. France. Bark contains 14 per cent. of tannin.

Q. coccifera, Kermes Oak. Fr. *Kermes, Garouille* (fig. 52). South Europe and Algeria. Root bark is called "rusque" or "garouille"; averages 10 to 18 per cent. tannin, but trunk bark does not exceed 11 per cent. This tree is the food of the kermes insect, used for dyeing scarlet before the introduction of cochineal.

Fig. 52.—Kermes Oak (*Quercus coccifera*).

Garouille is principally used in the South of France, giving a firm sole leather of a disagreeable odour and dark brown colour.

Q. Ægilops (and probably other species—*Q. macrolepis, græca, Ungeri, coccifera*), Valonia. Fr. *Valonée*; Ger. *Valonea, Ackerdoppen, Orientalische Knoppern.* Best Smyrna contains up to 40 per cent., Greek 19 to 30 per cent., Candia valonias up to 41 per cent., and Caramanian (probably not *Q. Ægilops*) 17 to 22 per cent. of tannins, which are at least principally pyrogallol derivatives, and which give blue-blacks with iron, no precipitate with bromine-water, and which deposit a great deal of bloom, consisting of ellagic acid.

Q. Ægilops (fig. 53) is said to be most abundant in the highlands of Morea, Roumelia, Greek Archipelago, Asia Minor, and Palestine, while *macrolepis* forms large forests in many parts of Greece, and especially on the lower slopes of Mount Taygetos. In Asia Minor the fruit ripens in July to August, when the trees are beaten and acorns left on the ground to dry. They are afterwards gathered, and carried on camels to stores in the towns, and thence by camel and rail to Smyrna, where they are placed in heaps 5 to 6 feet deep in large airy stores, and allowed to ferment and heat for some weeks, when the acorn, which contains but little tannin, contracts and falls from the cup, and is used for feeding pigs. This fermentation is risky, and if carried too far

Fig. 53.—Valonia Oak (*Q. Ægilops*).

the cups become dark coloured and damaged. The acorn contains a considerable amount of fermentable sugar.

When ready for shipment the valonia is hand-picked, the largest and finest cups (prima) going to Trieste, the second selection to England (Inglese), and the remainder, known as "natural," also coming largely to England. The "Inglese," although inferior in appearance to the very large selected cups, is of course less costly, and gives an equal yield of tannin.

In 1887 Smyrna exported about 23,000 tons to England and 16,000 tons elsewhere, principally to Austria, Germany, and Italy. The largest known crop is stated at 70,000 tons in Asia Minor and 14,000 in Greece, but the average yield is considerably less than this.

The beard contains considerably more tannin than the cups, sometimes over 40 per cent. It is often sold separately at the same or a lower price, and in Smyrna is known by the Turkish name *tirnac* (Ital. *trillo*).

In Greece the best valonia is collected (in April ?) before the cup is matured and whilst it still encloses the acorn, and is known as *chamada* (It. *camata* and *camatina*). The colour of these kinds is excellent and the percentage of tannin high. Mainly used by dyers, but often worth attention for tanning where colour is important. In *camatina* the acorn is completely covered in the cup, while in *camata* it is partly exposed.

The next quality, *rhabdisto*, is beaten down by sticks in September to October (hence name), while after the first rains the fruit falls and turns black, and is called *charcala*. It contains but little tannin, and is not generally collected.

Sometimes valonia is attacked by a sort of honeydew, probably caused by an aphis, which renders it very sticky, and perhaps more liable to heat, but does not in itself damage its tanning properties.

The lighter the colour, the heavier the weight, and the thicker the scales of the beard, the better the quality usually proves, but analysis is the best guide. Caramanian valonia is very inferior.

The tannin contained in valonia is especially valuable in the manufacture of sole leather. It deposits much bloom, and if used as a dusting material has the characteristic of making the leather solid and compact, but leaves the grain somewhat rough and hard to work. In mixture with gambier and other materials it is an excellent tannage for dressing leather, and with proper management deposits little or no bloom (*cp*. p. 364).

Q. infectoria (fig. 54) is the source of the "Turkish" or Aleppo galls. Galls are caused by insects, principally of the genus Cynips, or gall-wasps, which lay their eggs in different parts of plants, and in some way cause an abnormal growth of the bud, leaf, or other part. The gall-wasps affecting the different oaks are shown in the figures.

Aleppo galls are developed from the young shoot of the oak, are best before the insect has escaped, and contain in this stage up to 50 or 60 per cent. of gallotannic acid. When the insect has developed and escaped the galls are of course perforated, much lighter, and more porous. These galls and those of *Rhus semialata* are the principal sources of the tannin of commerce.

FIG. 54.—Gall Oak (*Q. infectoria*).

The *Q. infectoria* also bears a large gall like an apple, " Apples of Sodom," or " rove," caused by a different insect. This, in a crushed condition, has been somewhat largely used as a tanning material, and contains 24 to 34 per cent. gallotannic acid.

English oaks have several species of galls and oak-apples, but they do not seem to be of much value for tanning.

Knoppern are galls produced on the immature acorns of various species of oaks, principally *Q. cerris* in Hungary, and were formerly largely used there for tanning, as they contain up to 35 per cent. gallotannic acid. They are now less abundant, and have been largely replaced by valonia, sometimes called *orientalische Knoppern.* Like all purely gallotannic materials, they naturally give a soft and porous tannage, ill-adapted for sole leather purposes, which has led to the Austrian practice of drying, or rather stewing, the leather in very hot and damp stoves, which make it hard and brittle.

Chinese and *Japanese galls* are the product of the action of an aphis on a species of sumach, and will be mentioned again under sumachs (*Rhus*).

Djaft, dchift, jift, or *jaft* is a material apparently of Eastern origin, and said to be derived from an oak of Kurdistan. Dark red scales or fragments, origin uncertain, very astringent and darkish tannage; liquor when spilt dries whitish, apparently from crystallisation of some sort. It contains a large amount of tannin. It appears very irregularly in commerce, and the writer would be glad to obtain further samples and details of origin. He once used 6 or 7 tons successfully in sole leather tannage. It has also been attributed to a shrub allied to the *Cæsalpinias* (p. 327).

The most important American oaks are: *Q. prinus* (*castanea, monticola*), the Chestnut or Rock Oak (fig. 55). About equal to our oak in strength, bark very thick, and infusion strongly fluorescent, especially in presence of ammonia. Source of chestnut-oak extract. The most important tanning oak-bark of the United States.

Q. alba, or "white oak," is perhaps the most widely distributed and abundant of any of the American oaks, and very closely resembles the European *Q. robur.*

Q. tinctoria or *nigra*, Black or Quercitron Oak. Poor as a tanning material, but used for dyeing yellow and for modifying the colour of hemlock tannages. The dyestuff, *quercetin*, is closely allied to that of fustic, and gives yellows with alum and tin mordants.

A good deal of information is given by Trimble [1] on American oaks and other tanning materials.

Q. pachyphylla. Acorn cups used, very similar in appearance to Greek valonia. Tree grows in hilly districts of N. India.

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[1] *The Tannins*, vol. ii. Lippincott, Philadelphia, 1894.

Tannin gives strong but good colour. Analyses by Mr H. Brumwell show 13 to 15 per cent. tannin and 9 to 13 per cent. non-tannin in dry cups. Acorns (dry) showed 2·0 per cent. tannin and 5·6 per cent. non-tannin. The usual proportion of cups to acorns is about 70 : 30. The leaves and bark contain considerable tannin. According to Pilgrim 10 per cent. in the former and 12 to 13 per cent. in the latter.

FIG. 55.—Chestnut Oak (*Q. prinus*).

Q. fenestrata. N. India. Mature bark contains 15·8 per cent. tannin and 8·4 per cent. non-tannin (Pilgrim, calc. on dry material), and yields liquor of very light colour. It is suggested as suitable for extract manufacture.

Q. lineata. N. India. Twig bark contains 10·5 per cent. tannin and 11·0 per cent. non-tannin (Pilgrim, dry material), and is slightly richer than mature bark. Colour good.

Q. lamellosa. N. India. Leaves, twig bark, and mature bark contain 8 to 10 per cent. of tannin and 13 to 18 per cent. non-tannin (Pilgrim, dry material). The liquor has a strong but not red colour.

Other important Indian oaks are *Q. glauca* and *Q. incana*; bark of last said to yield 22 per cent. of tannin.

In addition to these, Dekker gives a large number of other oaks containing tannins, but mostly in quite small quantities, and rarely so much as 12 per cent. *Q. rubra* (common red oak of N. America) has twig-galls, in which Trimble found 34·8 per cent. tannin, but only found 4 per cent. in the bark, though Eitner found 16 per cent.

POLYGONACEÆ, Docks

The roots of most members of this family contain tannin, often in considerable quantity.

Rumex hymenosepalum, Canaigre, Gonagra (Cana agria), Red Dock, wild pie-plant (fig. 56). Common in sandy alluvial plains of Mexico and Texas, and considerably resembling rhubarb. Its tuberous roots resemble those of the dahlia, and contain, when air-dried, 25 to 30 per cent. of a catechol-tannin, probably allied to that of mimosa, but of a much paler and yellower colour. Undried, the roots contain about 68 per cent. of water and only 8 per cent. of tannin. When well harvested by slicing thin and rapidly drying it gives leather a bright orange colour and, it is said, considerable weight and firmness, and is thus specially suitable for use in retanning and finishing light goods and harness leather. Besides tannin, the root contains a yellow colouring matter and about 8 per cent. of starch, of which the granules are very variable in form and size, but mostly oval or elongated, and do not stain readily with iodine till they have been well washed or treated with dilute sulphuric acid. Both the starch and tannin are contained in large and somewhat thin-walled cells, and the sliced material is easily extracted at low temperatures. Greater heat gelatinises the starch and extracts a darker colour. The best temperature for extraction is between 30° and 50° C. (see p. 412). The large content of starch and the cost of culture and harvesting has told against the use of this plant. For a drum-tannage on Dr Turnbull's principles, however, the presence of starch would be no disadvantage (*cp.* p. 573).

The root is most readily grown from tubers or portions including the crown, as the plant seeds sparingly. Sandy soils, subject to inundation or irrigation, seem best suited to its culture. In California and Arizona the growth begins in October or November with the winter rains, blooming about the end of January, while

FIG. 56.—Canaigre (*Rumex hymenosepalum*). *New Commercial Drugs and Plants*, T. Christy.

the leaves die down in May and the roots remain dormant during the summer. It is not important at what time the roots are harvested, and they seem to improve in percentage of tannin up to the second year, after which they become darker and deteriorate.

The harvested crop should be sliced into thin pieces and rapidly dried at a low temperature, or, still better, converted at once into extract. This is already done on a considerable scale at Deming, New Mexico. The residue after extraction is used in America as cattle-food ; and might no doubt be also applied to the production of alcohol.

Planting takes place in autumn, in rows, say 30 inches apart, with 10 inches between each root. Roots for " seed " should be kept in the ground or stored in dry sand. This should yield a crop of 10 tons per acre in an average season.

References.—Report U.S. Commissioner of Agriculture, 1878, pp. 119 *et seq.* ; Trimble, *American Journ. of Pharmacy*, p. 395, 1889 ; *Canaigre,* Bull. No. 7, Arizona Agr. Expt. Station, 1893 ; *Canaigre or Tanner's Dock*, Bull. No. 105, University of California, Berkeley, Cal. ; *Canaigre Tannin,* Trimble and Peacock, Philadelphia, 1893 ; *Report to the German Leather Trades Association,* by v. Schroeder, 1894 ; *Il Canaigre,* E. Andrieis, Turin, 1899.

Rumex maritima. Central Europe, England, Ireland. It is said by de Lof to be found in California, where it is used by the Indians for tanning ; but he probably confounds it with canaigre. De Lof found its roots, wet, to contain 6 per cent., and after drying 22 per cent. of tannin, together with starch and an acid allied to malic.

Several English docks contain tannin ; the writer had a sample of leather tanned with dock-root (very possibly *R. aquaticus*), many years old, but still soft and close in texture, and of excellent quality.

Polygonum amphibium. Said to grow on thousands of acres (?) on the lower Missouri. Roots contain 22 per cent., branches 17 per cent. of tannin. *P. amphibium* is a common English and European plant, with spikes of pink flowers, growing in marshes and ponds. Probably this is the *Polygonum* analysed by Fraas, who found 20 to 26 per cent. tannin.

Polygonum Bistorta. Common in damp places in England. Bistort, Snakeweed, called " Eastermer giants " in Cumberland, where the young leaves are used for making herb-puddings. Fraas found 16 to 21 per cent. tannin in the roots.

Other species are known to contain much tannin. Perkin found a red colouring matter in *P. cuspidatum,* a native of India and China, commonly grown in gardens as a foliage plant (*Journ. Chem. Soc.*, 1895, p. 1084). *P. tinctorium*, used as a source of indigo in China and Japan.

Coccoloba uvifera, Seaside Grape of West Indies; source of West Indian kino. Whole plant rich in tannin.

Dekker also mentions *Coccoloba crescentifæolia* (Cham. and Schl.) of Brazil, which gives an astringent extract. A number of other species of *Polygonum* and *Rumex* contain tannins in unimportant quantities.

LAURACEÆ, Bay Family

Persea, or *Laurus lingue*. Bark used in Chili for tanning Valdivia leather. (According to Arata, *Laurus caustica*.) A tree 25 to 30 feet high and 2 feet in circumference. Bark rough outside and whitish, with an aromatic smell and taste, brittle and easily ground, contains 17 to 19 per cent. of a catechol-phloroglucol tannin, greening iron-salts (*Journ. Chem. Soc.*, 1881, p. 600); 22·0 per cent. tannin, 8·3 per cent. non-tannins (Pollak, *Coll.*, 17, 1918, p. 3). A large number of heavy hides are tanned yearly with this bark in Valdivia and district, and mostly sent to Hamburg. The hides are thick and scarcely tanned through, colour fair, leather soft and porous.

Persea Meyerina N. and *Laurus Pneumo*. Said to be also used in Chili.

According to Eitner, both these barks contain considerable quantities of starch. Many others of this family contain tannin, but mostly in small quantity.

MYRSINACEÆ

Myrsine gardneriana D.C. "Capororocca," Brazil, Rio Grande do Sul; bark largely used for tanning.

PROTEACEÆ

Banksia serrata, Heath Honeysuckle. Australia. Specimen examined contained 11 per cent. tannin; according to Maiden it reaches 23 per cent.

Banksia integrifolia. Queensland. Bark contains 11 per cent. tannin. Maiden found 10·8 per cent. tannin.

Grevillia striata. Australia. Bark contains 18 per cent. tannin, yielding reds.

Leucospermum conocarpum. Kruppelboom. Knotted Tree. Cape of Good Hope. Said by de Lof to contain 22 per cent. of tannin; but a specimen examined by the Author yielded 10·9 per cent. on analysis.

Protea mellifera. Sugarbush. *Suikerbosch.* Cape of Good Hope. Bark contains 25 per cent. tannin, according to de Lof; but Palmer found 18·8 per cent. Dekker only states 3 per cent.

Protea grandiflora. Waagenboom. Cape. Contains 25 per cent. tannin (de Lof); 15·9 per cent. (Palmer); 15·6 per cent. (Procter).

Protea speciosa. Cape of Good Hope. Used for tanning.

Leucadendron argenteum, Silver Tree, *Silverboom, Witteboom.* Cape of Good Hope. Bark said to contain 16 per cent. tannin (de Lof); a specimen examined by the Author yielded 9·2 per cent.

Brabium stellatifolium, Wilde Amandelboom, Wild Almond. Cape of Good Hope. Astringent.

SANTALACEÆ

Osyris compressa (*Fusanus compressus, Colpoon compressum, Thesium Colpoon*), "Cape Sumach," "*Pruim Bast,*" leaves and bark, Cape of Good Hope. Leaves contain about 23 per cent. (Perkin), 17 per cent. (Maiden) of tannin, and form a useful substitute for sumach; but the tannin is not identical, and is of the catechol class, resembling gambier.

O. arborea. Northern India. Leaves rich in tannin; 20 per cent.; contains quercetin (Perkin).

O. abyssinica. Somaliland. The leaf contains 23 to 25 per cent. tannin (Watter).

Fusanus acuminatus (*Santalum acuminatum*), "*Quandony.*" Australia. Eighteen to 19 per cent. dark-coloured tannin.

Exocarpus cupressiformis. Australia. Bark contains 15 per cent. tannin (Maiden).

DAPHNOIDÆ, Spurge Laurels

Daphne Cnidium L., "*Garou.*" Algeria. Used for dyeing and tanning.

PLUMBAGINÆ

Plumbago Europea, Leadwort. Fr. *Dentelaire.* A garden plant in England, native in France; contains much tannin, especially in the root-bark.

Statice coriaria, Marsh Rosemary. South of Russia. Roots up to 3 metres long and 2 to 12 cm. thick; used by Kalmucks for tanning sheep-skins; contain 22 per cent. of tannin (de Lof). Dekker gives 20 to 22 per cent.

S. gmelini W. South Russia. Used as above.

S. latifolia. Caucasus and Middle Asia. Strongly astringent.

S. scoparia Pall. Siberia. Strongly astringent.

S. limonum L., Sea Lavender. Coasts and salt marshes of Europe and America. Richer in tannin than *S. coriaria*; used in France, Spain, and Portugal.

Several other species contain tannin. These plants are allied to "Thrift" (*Armeria*), which is also astringent.

MALPIGHIACEÆ

Byrsonima spicata (Rich.). S. America, Antilles, "Tamwood." Bark contains up to 43·5 per cent. tannin.

B. coriacea. Jamaica, "Golden Spoon."

B. chrysophylla, etc.

B. crassifolia H.B.K. Cuba. Contains much tannin in bark and unripe fruit.

B. cydoniæfolia, var. *chiquitensis* (Juss.). Bolivia. Native name "mureci." Bark contains 20 per cent. tannin.

Malpighia punicifolia. Nicaragua, "Nancite"; "Mangrutta." Bark contains 20 to 30 per cent. of light-coloured tannin.

M. faginea (Sw.). Mexico, "Nance." Bark up to 26 per cent.

POLYGALACEÆ, Milkwort Family

Krameria triandria, Rhatany, Peru.

The root is used in medicine, and is stated to contain 40 per cent. of tannin.

Wittstein found only 20 per cent. of an iron-greening catechol-phloroglucol tannin allied to tormentil tannin in the root-bark, the only active part of root.

EUPHORBIACEÆ

Cleistanthus collinus, "*Kodarsi*," Deccan. Bark stated to contain 33 per cent. of tannin.

Phyllanthus emblica. (Aonla, Amla). India. Twig bark, mature bark, leaves, and immature fruit (emblic myrobalans) all contain considerable tannin. Analyses by Pilgrim and others as follows:—

	Leaves. Per cent.	Twig Bark. Per cent.	Fruit, without Stone. Per cent.
Tannin	23 to 28	19 to 24	26 to 35
Non-tannins	14 ,, 19	10 ,, 17	37 ,, 40

Twig bark gives smooth grain, steady swelling of hides during tannage. Reddish colour when used alone. Very useful material.

P. distichus and *nepalensis* both yield tanning barks.

ANACARDIACEÆ

Schinopsis balansæ (Engl.), also named *Quebrachia Lorentzii* and *Loxopteryngium Lorentzii*. Span. *Quebracho colorado*. South America, especially Argentine Republic; the highest proportion of tannin occurring in the wood from Gran Chaco district. Wood contains on an average about 25 to 28 per cent. of a red, difficultly-soluble tannin, yielding "reds," and containing catechol and phloroglucol. The tannin is not very soluble in water, and hence can only be used in weak or warm liquors, but is very astringent, and gives a firm, reddish leather. The wood also contains a catechin [1] and a colouring matter, fustin, identical with that of "young fustic." It is imported into England, and more largely to Havre and Hamburg, in logs, which are there chipped like logwood, and either used direct for tanning or made into extract. A very cheap tan. With alum it gives a yellow colour. The extract usually dissolves to a fawn-coloured turbid solution. Many quebracho extracts are now made completely soluble by treatment with alkaline bisulphites (*cp.* p. 404), or by treatment with alkali, which is afterwards neutralised. The so-called "insoluble" matter is really a sparingly soluble tannin, and if agitated with hide will tan it completely.

The Spanish word "quebracho" means "axe-breaker," and is applied to many hard woods. The wood of *S. balansæ* has a specific gravity of 1·27 to 1·38, and is consequently much heavier than water. It is much used for railway sleepers, for which it is very durable. The sapwood only contains 3 to 4 per cent. and the bark 6 to 8 per cent. of tannin.

The annual cut is said to be much less than the annual growth. It is common in Chili and Paraguay, as well as in the Argentine.

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[1] See *P. Arata, Journ. Chem. Soc.*, 1878, A, p. 986; 1881, A, p. 1152; and Perkin and Gunnell, *Trans. Chem. Soc.*, 1896, 1303.

(" Rep. on Tanning Materials of Latin America," T. H. Moran, Special Agents' Bulletins, No. 165, from *J.A.L.C.A.*, 14, 1918, p. 441.)

Aspidospermum quebracho (quebracho blanco) belongs to the *Apocynaceæ.* It contains but little tannin, but is valuable for an alkaloid, aspidospermin.

Schinus mollis, "Molle," Buenos Ayres. Leaves only used ; said to contain 19 per cent. tannin.

S. Aroeira, Brazil. Said to contain 14 per cent. tannin.

Pistacia lentiscus, Ital. *Pistacio*, Fr. *Lentisque.* Sicily, Cyprus, Algeria. Small myrtle-like leaves contain from 12 to 19 per cent. of a catechol-tannin, and are very largely used in the adulteration of sumach. Leather tanned with sumach adulterated with this material darkens and reddens on exposure to light and air, and for this reason its use in many cases is decidedly injurious. In Cyprus and the East it is known as "*Skens*," Ital. *Schinia*, Fr. *Poudre de Lentisque*, in England often called Cyprus sumach (*cp.* p. 309).

Fig. 57.—Sicilian Sumach (*Rhus coriaria*).

P. orientalis, terebinthus, vera, etc., India, Mediterranean. Yields various aphis galls, 30 to 40 per cent. tannin. A sample of galls of *Pistacia vera*, " *Gool-i-pista*," India, examined in the Author's laboratory, contained 30 per cent. of a light-coloured tannin.

Rhus coriaria, Sicilian sumach. Ital. *Somacco* (fig. 57). A shrubby bush, of which leaves and small twigs are used.

Mostly propagated by suckers from older plants, which are planted in rows about 2 feet apart in early spring, and pruned to 6 to 8 inches. Bushes begin to bear the year after planting, though the strength is not so good as from more mature plants. Cropping is either by pruning off shoots, or gathering leaves by hand ; in the latter case shrubs are pruned in winter. The leaves are dried either in the fields or on covered threshing floors, where they are afterwards separated from the stems by beating. Some is exported in this state as " leaf " or " baling " sumach, but most is ground to fine powder under edge-runners. " Ventilated" sumach is winnowed to remove dust and sand, which often contains iron. "*Mascolino*" is the best sumach from Palermo and district; "*feminella*" consists of weaker sorts from other parts, and is generally used for mixing.

The different varieties of sumach are classed as follows:—

	Relative Market Value.
Sumach for baling	2·5
,, for grinding	2·3
,, from yearling plants	1·5
,, from ends of branches collected in autumn	1·0

To prepare these different grades for ultimate consumption they are ground in mills similar to those employed for crushing olives, that is, in which two large stone wheels follow each other, revolving upon a circular bed, the whole construction being similar to the Spanish or Mexican *arrastre*. The sumach thus pulverised is passed through bolting-screens to separate the finer from the coarser particles.

After the sumach leaf has been subjected to the first process of trituration, the coarse remaining portions are re-ground and the product added to that which has been already obtained. The still unpulverised residue, known as *peduzzo*, is sifted, and the coarser and ungrindable parts are used as fuel, while the finer are mixed with the partially-ground, small, leaf-bearing branches (*gambuzza*, *gammuzza*), and ground again.

Palermo is the principal seat of the sumach trade. The material is generally bought from the small growers by middlemen, who hold it till market conditions are favourable. The quotations are always in *tarì* of 42·5 centimes per *cantar* of 79·342 kilos., which are obsolete even in Sicily, and have to be reckoned into *lire* (francs) and kilos. Consequently 1 tarì per cantar equals 0·53565 lira per 100 kilos.

In 1894, the prices delivered at the mills were about 41 to 42 tarì for mascolino, 37 to 38 tarì for feminella, 14 to 18 tarì for brusca, and 10 tarì for stinco per cantar, the lira being worth about 9d.[1]

Sumach has been introduced into Australia, and is said to thrive well in the dry plains of the Wimmera district.

Sumach often contains much sand, and sometimes particles of magnetic iron ore, which cause black stains, and may be collected by a magnet, and which dissolve in dilute hydrochloric

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[1] Cf *Kew Bulletin*, No. 107, pp. 293–6.

acid without evolution of hydrogen to a yellow solution. Metallic iron, which is also attracted by the magnet, dissolves in hydrochloric acid with effervescence to a colourless or green solution.

Good sumach contains at least 25 to 27 per cent. of tannin. The Author has analysed samples of undoubted genuineness containing as much as 32 per cent. of a tannin, allied to gallotannic, with some ellagitannic acid, and a colouring matter (myricetin) identical with that of *Myrica nagi* (p. 286), which gives yellows with alumina and tin mordants, and is fugitive to light.

Sumach is the best tanning material known for pale colour and soft tannage, and is hence used for moroccos, roans, skivers, etc., and also for brightening leathers of darker tannages, such as mimosa, gambier, the colouring matters of which warm sumach liquors seem able to dissolve.

In the report of the Society of Arts Committee on bookbinding leathers,[1] it is stated on abundant evidence that sumach-tanned leathers are less affected by light and gas-fumes, and less liable to decay, than those of any other known tannage.

Sumach is frequently adulterated with the ground leaves and twigs of *Pistacia lentiscus*[2] (" schinia " or " skens "), *Coriaria myrtifolia* (" stinco "), *Tamarix africana* (" brusca "), *Ailantus glandulosa*, *Vitis vinifera* (leaf of the common grape vine), *Cistus salvifolius* (L.), and some other species of the Rhus family, but *Pistacia lentiscus* is used to a much larger extent than any of the others. *Pistacia*, *coriaria*, and *tamarix* all contain considerable quantities of tannin, though less than genuine sumach, and of a different chemical constitution.

The most satisfactory method of detecting these adulterants is by microscopic examination, none of the chemical methods proposed being very satisfactory; though, as many of the added matters contain catechol-tannins, while those of sumach are purely pyrogallol derivatives, the method proposed by Hughes for the detection of quebracho in oakwood by the reaction of concentrated sulphuric acid might render good service, and any sumach infusion which was rendered turbid by bromine-water would at least be open to grave suspicion.

The most important work on the microscopic structure of the tissues of sumach and its adulterants was done by Andreasch, when during the later stages of his last illness he was obliged to winter in Sicily.[3] His work will well repay study, but unfortu-

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[1] *Soc. Arts Journ.*, 1901, p. 14.

[2] Adulteration has a good deal lessened, since it has been easily detected by the microscope.

[3] *Sicilianischer Sumach und seine Verfalschung*, Wien, 1898.

nately does not admit of useful abstraction here. A very useful investigation was also made in the Author's laboratory by Messrs M. C. Lamb and W. H. Harrison [1] as regards the treatment and examination of the leaf-cuticles, which renders the detection of mixture comparatively easy. For details, the original memoir must be consulted, but if the suspected sumach be gently warmed for a few minutes with strong nitric acid, its more delicate leaf structure is entirely destroyed, and after washing and neutralising with sodium carbonate the strong cuticles of the leaves of the more common adulterants, "schinia" (*Pistacia lentiscus*), "stinco" (*Coriaria myrtifolia*), "brusca" (*Tamarix africana*), and *Ailantus glandulosa*, are uninjured, and easily recognised. Examination is rendered easier by dyeing the cuticles, safranine, acid green, Bismarck brown, and naphthol yellow being suitable for the purpose. Mr Lamb's photographs of the cuticles are reproduced in figs. 59–66, but, if possible, it is most satisfactory to compare the suspected sample direct with known specimens of the adulterants.

FIG. 58.—American Sumach (*Rhus glabra*).

R. glabra, Southern States, U.S.A. (fig. 58). Very largely used in the States to take the place of Sicilian sumach. A sample collected by the late Professor Trimble, and analysed in the Leather Industries Laboratory, contained 25 per cent. of tannin, and produced a leather of very much darker colour than Sicilian, but this may be largely due to carelessness in its harvesting.

R. typhina, "staghorn" or Virginia sumach, contains 10 to 18 per cent. of tannin. A sample from same source as above contained 13 per cent.

R. cotonoides, U.S.A. The analysis of a sample of this material

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[1] "Sumach and the Microscopic Detection of its Adulterants," *Journ. Soc. Dyers and Colorists*, March 1899. *Cp.* also *Leather Chemists' Pocket Book*, p. 202.

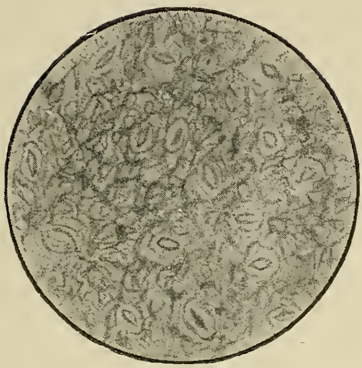

FIG. 59.—*Ailantus glandulosa.*

FIG. 60.—*Coriaria myrtifolia.*

FIG. 61.—*Colpoon compressa.*

FIG. 62.—*Rhus cotinus.*

gave 21 per cent. of tanning matter, and leather tanned with it was almost equal in colour to that from *R. glabra.*

Other sorts found in States: *R. semialata* (5 per cent. tannin); *R. aromatica* (13 per cent. tannin); *R. metopium* (8 per cent.); *R. copallina, R. pumila, R. canadensis*; *R. toxicodendron* is the well-known "poison ivy," a climbing plant which causes a severe and irritating eruption if touched.

R. glabra and *R. copallina* are chiefly recommended for extended cultivation in the United States.

In Virginia the leaves are collected and cured by the country people, and sold and delivered to owners of mills for grinding. Their particular object being to secure the largest possible quantity of product at the lowest cost, little attention is given to the quality obtained or the manner of collecting. The most intelligent dealers in the raw material urge upon collectors to observe the following particulars:—To ensure a maximum value for tanning purposes, the leaf should be taken when full of sap, before it has turned red, has begun to wither, or has been affected by frost. Either the leaf-bearing stems may be stripped off, or the entire stalk may be cut away, and the leaves upon it allowed to wither before being carried to the drying-shed; but care must be observed that they are neither scorched nor bleached by the sun. When wilted, they are carried to a covered place, and spread upon open shelving or racks to dry, avoiding the deposit in any one place of a quantity so great as to endanger the quality of the product by overheating and fermentation. Sumach should be allowed to remain in the drying-house for at least one month before sending to the market; in case of bad weather, a longer period may be required. When ready for packing for shipment it should be perfectly dry and very brittle, otherwise it is likely to suffer injury in warehouses from heating and fermentation.

Buyers of sumach leaves for grinding depend largely upon colour for the determination of the value; the leaves should, therefore, when ready for market, present a bright-green colour, which is evidence that they have suffered neither from rain after being gathered, nor from heating during the process of drying. Leaves having a mouldy odour or appearance are rejected. The Virginian crop reaches 7000 to 8000 tons, and is collected at any time between 1st July and the appearance of frost.

There is an important difference in the value of the European and American products. The proportion of tannic acid in the latter is generally lower than that found in the former, which is much preferred by tanners and dyers. By using Sicilian sumach it is possible to make the finest white leathers, while by

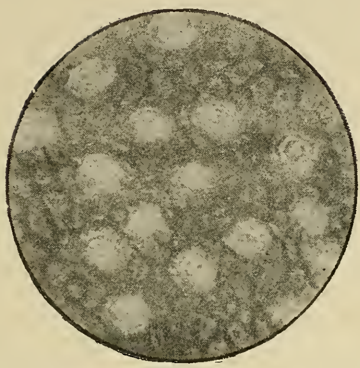

FIG. 63.—*Pistacia lentiscus.*

FIG. 64.—*Rhus metopium.*

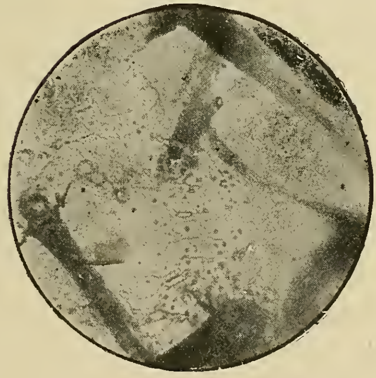

FIG. 65.—*Rhus coriaria.*

FIG. 66.—*Tamarix africana.*

the employment of the American product the leather has a disagreeable yellow or dark colour, apparently due to a colouring matter which exists in larger quantity in the American variety than in the Sicilian.

Experiments upon the presence of colouring matters made by treating an infusion of sumach with a solution of gelatine gave the following results :—

Virginia,	mixed,	collected in	June, gave	A nearly white precipitate.
,,	,,	,,	July, ,,	A decidedly yellowish-white precipitate.
,,	*R. copallina*	,,	August ,,	A dirty-yellow precipitate.
,,	*R. glabra*	,,	,, ,,	A very dirty-white precipitate.
Fredericksburg,	mixed	,,	,, ,,	A dirty-yellow precipitate.
Sicilian		,,	,, ,,	A slightly yellowish-white precipitate.

For the purpose of tanning white and delicately coloured leathers, therefore, the collection should be made in June ; while for tanning dark-coloured leathers, and for dyeing and calico-printing in dark colours, where the slightly yellow shade will have no injurious effect, the collection may be made in July. It appears that, for all purposes, the sumach collected after the 1st of August is inferior in quality.

Experimental results as regards percentage of tannin obtained by collecting sumach at different seasons showed :—

				Per cent. of Tannic Acid.
Virginia,	mixed,	collected in	June, gave	22·75
,,	,,	,,	July ,,	27·38
,,	*R. glabra*	,,	August ,,	23·56
,,	*R. copallina*	,,	,, ,,	16·99
Sicilian,	*R. coriaria*	,,	,, ,,	24·27

It is evident, therefore, that in order to secure the maximum amount of tannic acid the sumach should be collected in July, but the colouring matter of the leaves has an important influence upon the value of the product. The leaves of the upper extremities of the stalks are always richer in tannic acid than those of the base; and the increase of age of the plant is accompanied by a general diminution of this acid.

The mill used for grinding sumach leaves consists of a heavy, solid, circular, wooden bed, 15 feet diameter, with a depression around the edge a few inches deep and 1 foot wide, for the reception of the ground sumach from the bed, and two edge-rollers, weighing about 2500 lb. each, 5 to 6 feet diameter, and provided with numerous teeth of iron or wood, thickly inserted. In Europe and in some parts of the Southern States sumach is still ground by stones revolving on a stone bed, and the sifting is often done by hand.

R. cotinus, Venetian sumach. Fr. *Arbre à perruques*; Ger. *Perrukenstrauch* (fig. 67). In Europe it grows in the Apennines, but is said to be common in the West Indian islands. More important as a dyeing than as a tanning material, its twigs and wood, "young fustic," containing a large proportion of a colouring matter (fisetin), which with tin and alumina mordants dyes bright yellows; and much resembles, but is not identical with, the myricetin present in *R. coriaria*.[1] Its leaves, known as Turkish or Venetian sumach, contain about 17 per cent. of tannin, and are used for tanning.

FIG. 67.—Venetian Sumach (*Rhus cotinus*).

R. pentaphylla, "Tezera," Algeria, is used by the Arabs for tanning goat-skins.

R. Thunbergii, *Kliphout*, Cape of Good Hope. A sample of the bark analysed in the Author's laboratory contained 28 per cent. of tanning matter. A valuable tanning material, of reddish colour. The tannin is of the catechol class.

Several other species of Rhus are used in tanning. *R. semialata* yields Chinese and Japanese galls, containing up to 70 per cent. gallotannic acid. They are caused, not by a fly, but by the attack of an aphis, as are those of the allied

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[1] Perkin and Allen, *Trans. Chem. Soc.*, 1896, 1299.

Pistacia.[1] The asphides pass their asexual stage inside the gall, which is large and thin-walled. A similar aphis-gall is found on the American sumach.. A specimen of the leaves examined at Leeds University yielded only 5 per cent. of tannin.

R. succedanea (L.). India. Leaves said to contain 20 per cent. tannin.

R. Mysorensis. S. India. Bark gives pink colour to chromed hide powder, and is a pyrogallol tannin. Analysis (Pilgrim, dry material), tannin 19·5 per cent., non-tannin 11·4 per cent. on dry material.

Mangifera indica, Mango, widely distributed in the Tropics. Bark and leaves rich in tannin, which gives green-blacks with iron.

CORIARIACEÆ

Coriaria myrtifolia, French sumach (of which there are four kinds—*fauvis, douzère, redoul* or *redon,* and *pudis*). A poisonous shrub of South of France; leaves used for tanning, and as a sumach adulterant under the name of "stinco"; contain about 15 per cent. tannin (*cp.* p. 309).

C. ruscifolia bark, the *tutu* of New Zealand, contains 16 to 17 per cent. of tannin.

C. nepalensis (Wall), Eng. India. Leaves 20 per cent., all parts rich in tannin.

Other Coriarias merit examination, and are known to contain much tannin.

RUBIACEÆ

Rubia, Madder, allied to Galiums, which are almost the only English representatives of the family. The coffee- and cinchona-plants are foreign representatives.

Nauclea (or *Uncaria*) *gambir.* East Indies (fig. 68). A climbing shrub, source of "gambier," or "Terra Japonica"; also called "Catechu," in common with several other solid extracts. Gambier is first described by the Dutch trader Couperus in 1780; plant introduced in Malacca, 1758; plantations established in Singapore in 1819.

Culture is mainly by Chinamen, and is very rude; it yields rapid return, but under the treatment to which it is subjected a plantation is worn out in ten to fifteen years. Cropping commences three years after planting, and is continued two to four times annually with little regard to fitness of shrubs, the plant

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[1] See Flückiger and Hanbury, *Pharmacographia.*

being cropped till it has barely leaves left to support existence. It is found advantageous to combine pepper-culture with that of gambier; the spent leaves form a good protection for the pepper-plant roots, but they have little actual manurial value.

Cropping is done with a knife called a *parang*, while a larger knife is used for chopping the leaves and twigs before they are put in a boiler, in which they are heated with water till the liquid, which is constantly stirred during the operation with a wooden five-pronged stirrer, becomes syrupy. The leaves are then brought out with a wooden fork, and allowed to drain on a tray, so that the liquor runs back into the boiler. The coarser matter still remaining in the boiler is removed with a strainer like a racquet, and the finer by straining the liquor through a perforated cocoanut shell into small shallow tubs, where it is allowed to cool with constant stirring with a cylindrical wooden bar, which

Fig. 68.—Gambier Shrub (*Nauclea gambir*).

is worked up and down with a rotary motion until the catechin crystallises. When quite cool the pasty mass is turned out of the tub, cut into cubes with sides 1 inch long with a hoop-iron knife, and dried on bamboo trays in racks under sheds, or sometimes smoke-dried with wood fires.

Good cube gambier is an earthy-looking substance, and is dark outside, but pale within from crystallisation of catechin. Catechin is not itself a tanning material, but is apparently converted into a tannin by drying at 110° to 126° C., when it parts with a molecule of water. It is very probable that a similar change occurs in the tannery. The tannin is a catechol-phloroglucol derivative, less astringent than most of this series, and of pale colour (see p. 339).

A commoner quality, called " block-gambier," instead of being cut into cubes, is run into large oblong blocks of about 250 lb. weight, which are wrapped in matting and exported in a pasty condition. These contain 35 to 40 per cent. of tannin, as estimated by the hide-powder method, while the best cubes reach 50 to 65 per cent. Besides the forms named, various others are made, principally for native use in chewing with betel-nut in the form of small biscuits, or in thin discs (" wafer gambier ") by running the pasty mass into bamboos and cutting the cylinder so formed into thin slices. These forms are usually light in colour, and very rich in catechin.

For details of the chemistry of gambier see *L.I.L.B.*, 157.

Uncaria acida (Roxb.). Moluccas, Java.

U. Bernaysii (F. v. M.). New Guinea.

U. dasyoneura (Thwaites). Ceylon. Are said also to yield gambier

APOCYNACEÆ

Carissa spinarum (Karunda). C. and N. India. Bush. Leaves used in mixture. Analysis (Brumwell), tannin 8·0 to 11·5 per cent., non-tannins 13·5 to 15·0 per cent. Not very easily absorbed by hide. Infusion pale in colour and of extreme swelling power. According to Fraymonth and Pilgrim produces very tough leather.

Aspidospermum quebracho. Sp. *Quebracho blanco*. Brazil. Bark contains aspidospermin, an alkaloid used in medicine, but both bark and wood are poor in tannin.

Quebracho colorado, see ANACARDIACEÆ, p. 306.

ERICACEÆ, Heath Family

Arctostaphylos (or *Arbutus*) *uva-ursi*, Bearberry. Used in Russia, Finland; twigs and leaves said to contain 14 per cent. tannin. Often adulterated with leaves of *Vaccinium vitis-idæ* or Cowberry.

Arbutus unedo, Common Arbutus. Leaves, fruit, and bark used on Mediterranean coasts.

VACCINIÆ

Vaccinium Myrtillus, Bilberry. Used in Piedmont.

SAXIFRAGEÆ

Weimannia glabra L., "Curtidor" bark. Venezuela.

W. macrostachys D.C. Reunion.

W. racemosa, New Zealand Towai or Tawheri bark.

These species contain 10 to 13 per cent. of iron-blueing tannin, and have been practically used, but are not of much importance.

TAMARISCINIÆ

Most of the members of this group are poor in tannin, but several species have galls which are rich.

Tamarix africana, Egypt, Algeria. Galls containing 26 to 56 per cent. tannin. The small twigs are collected in Tunis, and when dried and ground are imported into Sicily to be used for the adulteration of sumach under the name of "Brusca," and contain about 9 per cent. of tannin (*cp.* p. 310).

T. articulata, Morocco. Yields galls produced by aphides, called in Arabia *Takout*, and stated by Vogel to contain 43 per cent. of tannin.

T. gallica. Used in Spain and Italy.

OXALIDEÆ

Oxalis gigantea, source of *churco* bark, Chili. A thin, brittle, dark red bark, mostly about 2 mm. thick, cork and ross entirely absent. The bark is brittle, and the cells thin. It contains about 25 per cent. of an easily extracted, dark red tannin, giving green-blacks with iron. The bark has been incorrectly attributed to *Fuchsia macrostemma*. (*Cp.* Von Höhnel, *Die Gerberinden*, p. 125, and this book, p. 324.)

COMBRETACEÆ

Several families of this genus contain trees rich in tannin, but most important are the Myrobalans (often, but incorrectly, written Myrabolams or Myrabolans), the unripe fruit of various species of Indian *Terminalia*.

Fig. 69.—Myrobalan Tree (*Terminalia Chebula*).

Terminalia Chebula (fig. 69), a tree 40 to 50 feet high, and yielding good timber, is the source of all the ordinary varieties, which differ only in the district from which they are obtained and the state of maturity of the fruit. The nuts contain from 30 to 40 per cent. of tannin. Of the various sorts, probably those known as Bombays are least unripe, while " lean greens " are the most so. The unripe fruit is the richest in tannin. " Bombays " have a smooth skin in coarse wrinkles, and when cut are porous and light coloured. " J's " (Jubbalpores) and " V's " (Vingorlas) have finer and shallower wrinkles, and are harder, solider, and consequently darker looking, but do not give a darker liquor; while "lean greens" are greener, have less yellow colouring matter, and consequently more nearly approach in character to sumach, which the tannin in many respects resembles, though probably containing more ellagitannic acid in proportion to gallotannic acid than the latter.

The "nuts" should be bright in colour, not worm-eaten, nor "waxy" or soft. If kept in a damp place they rapidly absorb moisture and fall into the "waxy" condition, in which they are very difficult to grind, sticking to and choking the cutters or beaters of the mill.

Neither the large hard stones nor their kernels contain tannin, but the latter have an oil which gives a peculiar odour to leather. The tannin exists in large and rather thickly-walled cells, and is not very easily extracted; the skin is wrinkled, but the uncrushed nuts swell up to their original plum-like form when placed in water for some time. The bark is almost as rich as the fruit, and the tree also yields galls.

T. Belerica yields Beleric or "Bedda nuts," which are downy, rounder and larger than ordinary myrobalans, and contain about 12 per cent. of tannin, used as adulterant of ground myrobalans. A sample of solid extract made from the bark of *T. Belerica* contained 70 per cent. of tannin.

T. tomentosa has downy nuts, containing about 10 per cent. of tannin; bark stated by de Lof to contain 36 per cent. of tannin. A sample of solid extract contained 56 per cent. of tannin. The bark contains about 11 per cent.

There are several other Indian species.

T. Catappa, "Badamier bark" of Mauritius, contains 12 per cent. of tannin.

T. mauritiana, "Jamrosa bark," said to contain 30 per cent. of tannin.

T. Oliveri, Malay Archipelago, yields "Thann leaves," from which an extract is made as a cutch substitute. A sample of the extract from Burmah examined recently in the Author's laboratory contained 62 per cent. of tannin. The tannin is a catechol derivative, differing from that of *Acacia catechu* in containing no phloroglucol (p. 330).

A sample of bark from Mandalay contained 31 per cent. of tannin, while the leaves from the same tree contained 14 per cent.

T. arjuna. (Kahua.) C. India. Bark gives 18 to 24 per cent. tannin (Pilgrim). Light fawn-coloured leather. Bark suitable for harness and sole-leather tannage. Apparently mixed tannin.

T. braziliensis (Eichl.). Brazil. Used for tanning.

T. Buceras (Wright). Antilles. Used for tanning.

A number of other species of *Terminalia* are rich in tannin.

Laguncularia racemosa (Gartn.) (*Conocarpus racemosus* L.). West Indies, Brazil, Jamaica, West Africa, "White mangrove," "Paletuvier gris." Very rich in tannin.[1]

Anogeissus latifolia. (Dhawa, Dhaura.) C. and S. India. Bark and leaves rich in tannin. Dhawa twig bark shows (Pilgrim) 13·5 per cent. tannins and 13·7 per cent. non-tannins; the mature bark 15·5 per cent. tannins and 8·8 per cent. non-tannins. Used in mixture. Leaves show (Pilgrim, Brumwell, and others) 10 to 18 per cent. tannin and 12 to 23 per cent. non-tannin. Immature leaves or shoots (Dhawa sumach) yield 20 to 30 per cent. tannin and 12 to 16 per cent. non-tannin. Red tips of immature shoots, separately collected in S. India, showed 54 per cent. tannins and 14·5 per cent. non-tannins. Mixture of bark and leaves tans quickly, giving pale, greenish leather. Good bleacher like European sumach. Used as a dye. Gives little swelling.

The tree grows like a true mangrove in the water on marshy coasts and the borders of large rivers. The bark is often mixed with other rhizophore barks in extracting, but would give a very superior tanning extract if it could be extracted separately.

RHIZOPHORACEÆ, Mangles or Mangroves

Rhizophora Mangle, and other allied species, Mangrove or Mangle, *Manglier, Paletuvier, Cascalote,* grows on tropical coasts all round the world. The barks vary much in strength, from 15 up to 40 per cent. in different species (see *Ceriops*). Leaves, used in Havana, are said to contain 22 per cent. tannin. According to Eitner, the younger plants contain the highest proportion of tannin. *R. Mangle* seems to yield a bark inferior to several other species. From their mode of growth most mangrove barks contain salt.

All trees growing in swamp, and of the same character of growth as mangrove, are called "Bakau" in the East Indies (*anglice,* mangrove), and various species of *Ceriops* yield the best tanning bark. A tidal mangrove swamp at low water is a tangle of arched roots like inverted branches on which the trees are supported.

The catechol-tannin, which is easily extracted, is of deep red colour and allied to that of the mimosas. In admixture with

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[1] Nierenstein and Webster, *Quart. Journ. of Com. Research in Tropics,* i. p. 70, v. p. 35, and *Collegium,* 7, 1908, p. 161.

other materials the red colour has a much smaller effect; the mangrove bark is now largely used in combination with pine, oak, and mimosa, and also with the synthetic tannins. The tannin does not diffuse appreciably through parchment paper, and salt can be removed in this way, but does not seem to do much injury in tanning.

Several other species are also rich in tannin, and used in different parts of the world under the name of mangle, as are also several species of *Conocarpus* belonging to the *Combretaceæ*.

Rhizophora mucronata. India and Burmah. Bark varies considerably; David Hooper, Indian Museum, Calcutta, gives 26·9 per cent. of tannin. Dr Koerner (Deutschen Gerberschule, Freiberg) analysed two samples in 1900, one containing 48 per cent. and the other 21 per cent. of tannin; two samples from the British Imperial Institute recently examined by the Author showed only 4·5 and 6·1 per cent. of tannin respectively.

Ceriops Candolleana, *Bakau* or *Tengah* Bark, East Indies. *Goran*, Bengal, South America. Contains up to 40 per cent. of tannin, and yields an extract which promises well as a substitute for cutch, to which, for dyeing purposes, it is nearly or quite equal. The solid extract contains up to 65 per cent. tannin, making a good but dark red leather.

Ceriops Roxburghiana, a somewhat larger tree, also growing in the Sunderbans; bark very similar in strength and character to the above.

Brugniera Rhumphii, the commonest mangrove on the coasts of New Caledonia,[1] has a hard red wood, little subject to decay. The leaves are oval, and 15 to 20 cm. long, and the fruits are shaped like cigars, but 35 to 40 cm. long, and when they drop fall point downwards into the mud, where they germinate. (The fruits of some mangroves germinate on the trees before they fall.) Thuau found 42·6 per cent. of tannin in the trunk bark, but only 12 per cent. in that of the aerial roots.

Crossostylis multiflora, "petit palétuvier," *ibid.*, New Caledonia, is a bush-mangrove, which often forms impenetrable thickets on the coasts and river banks. Its bark and twigs contain but little tannin, but the larger wood reaches 21 per cent.

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[1] U. J. Thuau, "Tanins de la Forêt Calédonienne," *Collegium*, 7, 1908, p. 376.

LECYTHIDACEÆ

Couratari domestica or *estrellensis*. Brazil.

C. legalis. Brazil, " Jiguitiba rose ;" large forest tree. Bark contains tannin.

C. guianensis. Guiana. Bark " de mahot couratori ; " used for tanning.

Lecythis pisonis (Cambes). Brazil, " sapucara " ; used by natives.

Many other species of Rhizophora, Ceriops, and Bruguiera yield barks containing good percentages of tannin.

ONAGRACEÆ, the Œnothera Family

Fuchsia excorticata, the only deciduous tree of New Zealand. Contains 5 per cent. tannin.

Fuchsia macrostemma. Chili. Yields Tilco or Chilco bark. Churco bark has been incorrectly attributed to this plant, but it is certainly derived from an *oxalis*, as stated by the Kew authorities. (*Cp.* Von Höhnel, *Die Gerberinde*, p. 125.)

Ludwigia caparossa, " Caparossa," Brazil. Bark 20 to 25 per cent. tannin. Abundant in Minas-Geraes and Goyaz.

GUNNERACEÆ

Gunnera scabra (*Pangue* ?), *Pauke*, Chili. Used occasionally in the tanning of goat-skins.

MYRTACEÆ

Eucalyptus globulus, and other species of *Eucalyptus*, common in Australia, and introduced into Algeria and Southern Europe (gum-trees), are more or less rich in catechol-tannins, their sap being the source of Botany Bay or Australian kinos, which contain up to 79 per cent. tannin. Several species of *Eucalyptus* afford astringent extracts; those from the " red," " white," or " flooded " gum (*E. rostrata*), the " blood-wood " (*E. corymbosa*), and *E. citriodora*, being quite suitable for replacing the officinal kind. The gum is chiefly obtained by woodcutters, being found in a viscid state in flattened cavities in the wood, and soon becoming inspissated, hard and brittle. Minor quantities are procured by incising the bark of living trees ; a treacly fluid yielding 35 per cent. of solid kino on evaporation is thus obtained. The gum is imported from Australia, but there are no statistics to show in what quantity.[1]

Eucalyptus longifolia bark, the "woolly-butt" of Australia; contains 8·3 per cent. of tannic acid, and 2·8 of gallic. The "peppermint" tree contains 20 per cent. of tannic acid in its bark. The "stringy-bark" (*E. obliqua*) gives 13½ per cent. of kinotannic acid. The Victorian "iron-bark" (*E. leucoxylon*) contains 22 per cent. of kinotannic acid, but is available only for inferior leather.

E. Occidentalis, "Mallet," "Flat-topped Yate," yields the valuable mallet bark, containing up to 44 per cent. of a yellow-brown tannin free from the red of the mimosas. Tannin 39·9 per cent., non-tannin 8·1 per cent. (Pollak, *Coll.*, 17, 1918, p. 3). It is most abundant in Western Australia. Used alone it gives a leather somewhat hard and inclined to brittleness, but is quite satisfactory in mixture with milder materials.

Myrtus communis, and several other myrtle species, contain a considerable amount of tannin in the bark and leaves.

Eugenia braziliensis (Lam.). Paraguay. Bark stated to contain 43·4 per cent. tannin; leaves, dry, 16·6 per cent., wood, 11·6 per cent. (Stockberger, 1912).

E. or *Sizygium jamjolana*. India, and cultivated in Antilles. Fruit "jamoon" or "Java plum." Bark 19 per cent. tannin (Hooper).

E. michellii (Lam.). Paraguay. Bark 28·5 per cent. tannin (Stockberger).

Stermolepsis gummifera. New Caledonia. Yields resinous matter with 80 per cent. tannin according to Heckel and Schlagdenhauffen; Thuau (1908) found 42·7 per cent. in resin, and 17·4 per cent. in bark.

SAPINDACEÆ

Mostly climbing shrubs, usually rich in saponin, and often containing tannin.

Cupania uraguensis. Paraguay. Bark 17·5 per cent. tannin (Stockberger, 1912).

C. spec. Paraguay, "cedrillo." 15·8 per cent. tannin (Stockberger).

Paullinia sorbilis or *cupana*. Brazil and Columbia; fruit "Guara," possibly identical with "cascalote," is very rich in tannin; said to contain up to 55 per cent. T. Callan found 43 to 48 per cent. tannin, 23 per cent. non-tannins. (See

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[1] Compare *Journ. Soc. Chem. Ind.*, 1902, p. 159.

J.A.L.C.A., 1915, pp. 241, 646.) Appears to be a mellow pyrogallol-tannin; develops acidity in liquors, and gives crimson colour with concentrated H_2SO_4.

P. multiflora. Paraguay. Is also rich in tannin.

RHAMNACEÆ

Zizyphus Xylopyra. (Gothar, Ghout). C. India. Fruit, in appearance like a small plum, contains a hard stone. Flesh and stone about equal in weight. Tannin contained in fruit, which also yield much glutinous or starchy matter, rendering filtration difficult. Said to give cracky leather if used in large proportion. Penetrates quickly. Liquor ferments rapidly and then acts as a bate. Very abundant and cheap. Analyses (Brumwell) of flesh, 23 per cent. tannin and 41·5 per cent. non-tannins.

Ceanothus velutinas. Colorado, California, "Snow-Bush." Leaves contain 17 per cent. of a catechol-tannin, and 7 per cent. of a brittle wax soluble in petroleum spirit (*J.A.L.C.A.*, 1916, p. 319).

GRANATACEÆ (PUNICACEÆ)

Punica Granatum. Pomegranate. Rind of fruit used in Spain and the East. Substitute for sumach. Analyses (Brumwell) show 27 to 30 per cent. tannin and 18 to 20 per cent. non-tannin on dry material. Bark of tree said to contain 22 per cent. of tannin. *Balaustines,* wild pomegranates, E. Indies, up to 46 per cent. tannin in fruit.

ROSACEÆ

Tormentilla erecta, Potentilla tormentilla. Root variously stated to contain 20 to 46 per cent. tannin. Red-coloured leather, formerly used in Orkneys, Shetland, and Faröe Islands, and in some parts of Germany.

Sorbus or *Pyrus Aucuparia,* Mountain Ash. Bark said to be stronger than oak.

Many other plants of the family contain tannin, among others the strawberry.

PAPILIONACEÆ

Butea frondosa.[1] This (with *Pterocarpus marsupium*)[2] furnishes East Indian kino. The flowers are used in India as a

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[1] *Dictionary of Economic Products,* I.B., p. 944; Hummel and Cavallo, *Proc. Chem. Soc.*, 1894, p. ii.

[2] *Agricult. Ledger,* 1901, No. 11, Government Printing Office, Calcutta.

yellow dye under the name of Tesu. Bark fairly rich in tannin.

Pterocarpus or *Drepanocarpus senegalensis* is the source of African kino, which contains up to 75 per cent. of tannin.

Cæsalpinia coriaria, Divi-divi. A tree of 20 to 30 feet, native in Central America, introduced successfully in India, but principally imported from Maracaibo, Paraiba, and Rio Hache. In Curaçoa it is a large tree up to 21 inches diameter, with dark and very hard and heavy timber. In Venezuela the local name is " nacasae " or " wouta pana." The dried pods contain 40 to 45 per cent. of a pyrogallol-tannin, mainly ellagitannic acid, and would be a most valuable tanning material but for a liability to fermentation and sudden development of a deep red colouring matter. The causes are not well understood, but apparently the risk can be materially lessened by use of antiseptics, and the writer, who has used a good deal, has never seen a case. If used in strong liquors it gives a heavy and firm leather, but is principally employed as a partial substitute for gambier on dressing leather. Used in rapid drum-tannage for light leathers an excellent colour may be obtained. It is said to give an especially firm and glossy flesh. Leather tanned with it, even when of outwardly good colour, has often a blueish-violet shade within, perhaps due to the development of a colouring matter allied to that of logwood. The seeds do not contain tannin, which lies almost free in the husk of the pod. The pods are about 3 to 4 cm. long, dark outside, and curl up in drying to an S-shape.

If passed through a disintegrator to break the pods a very rich tanning powder can be sifted out, mostly soluble in water.

C. digyna, tari or *teri* pods. Occurs in Prome, Toungoo, Bassin, Mynang, and other parts of India and Burmah, where it is used as a drug. The pod-case is said to yield over 50 per cent. of tanning matter. A sample from Burmah, kindly sent by the Imperial Institute, examined by the Author in 1900, contained 24 per cent. of tannin, but after removing the seeds the remaining pod-cases yielded 44 per cent. of tannin on analysis. *C. digyna* promises to become a valuable tanning material if it proves free from the tendency to ferment which is so troublesome in divi-divi. It has been introduced into England under the name of " white tan," which yields a leather quite as white as sumach ; but the supply seems at present uncertain.

C. cacolaco, Cascalote, Mexico. Pods rich in tannin (up to 55 per cent., Eitner). Pods larger and fleshier than divi, seeds smaller, tannin similar.

The pods of several other *Cæsalpinias* are used in tanning, sometimes under the name of "Algarobilla," which is simply a diminutive of Algaroba, the carob, or locust-bean, derived from

FIG. 70.—Algarobilla (*Cæsalpinia brevifolia*).

Arabic *al Kharroba*, and applied to several small pods. (See *Balsamocarpon* and *Prosopis*.)

C. (or *Balsamocarpon*) *brevifolia*, Chili, ordinary Algarobilla (fig. 70).[1] One of the strongest tanning materials known, containing an average of 45 per cent. of a tannin very like that of divi, but less prone to discoloration. The tannin lies loose in a

[1] *New Commercial Drugs and Plants*, No. 5, T. Christy.

very open skeleton of fibre, and is easily soluble in cold water; the seeds contain no tannin. If not allowed to ferment it produces a very bright-coloured leather.

Algarobilla has been attributed to *Prosopis pallida*, but this appears incorrect. Several species of *Prosopis* are known to yield tanning pods; those of *P. Stephaniana* of the desert of Kaschan, in Persia, are *dschigh dschighe*, perhaps identical with *dchift* or *jaft*. (See p. 298.) Bark of *P. spicigera* used in Punjab.

C. (or *Hæmatoxylon*) *campechianum*, Logwood. Central America. In addition to colouring matter, and a glucoside which it yields on oxidation, this wood contains about 3 per cent. tannin. Its principal use is in dyeing blacks with iron or chrome mordants. (See p. 493.) Trees ("Bastard Logwood") occur, apparently of the same species, but devoid of colouring matter.

C. tinctoria (?), "Cevelina" or "Celavina." Central America and western South America. Pod very rich in almost white pyrogallol-tannin; gives no bloom.

C. echinata yields "Brazil-wood." (See p. 505.)

C. Sappan, Sappan-wood, India.

Cassia auriculata, Turwad, Avaram, or *Tanghadi* bark, Southern India. Used for tanning so-called "Persian" sheep and goatskins; contains about 17 per cent. of a catechol-tannin. Leather tanned with it is of a pale yellow colour, but rapidly reddens in sunlight (*cp.* p. 498). The bark is small and thin, and curls up like cinnamon, hence its name cassia. It is one of the most important materials of India, but somewhat costly as compared to babul.

Cassia fistula (Amaltas, Sonari, Konnai). S. India. Bark contains up to 14·5 per cent. tannin, 16·0 per cent. non-tannins (Brumwell). Gives smooth-grained almost white leather. Usually employed in mixture with turwad or babul. Husk of pod contains 17 per cent. of tannin. Pulp of pod used as an aperient.

C. elongata and *lanceolata*. Senna leaves. Upper Egypt.

C. Sophora, "*Bali-babilan.*"

Peltophorium dubium. Paraguay. Bark 31·2 per cent. tannin.

MIMOSEÆ, a Tribe of Leguminosæ

Acacia arabica, "Babool," "Babul," India, "garad" or "Sunt" pods, Sudan, "Gambier pods" (fig. 71). Bark contains about 12 to 20 per cent. of catechol-tannin; one of the principal Indian tanning materials, used for kips and heavier leathers. Pods, used in India for bating, contain about same amount of tannin as bark, but of a different kind, that of the bark being a catechol-tannin, with a good deal of red colouring matter, while the pods contain a paler tannin allied to divi, which is not precipitated by lime-water. In Egypt the pods are called *bablah*, a name which is also applied to pods of *A. cineraria* and *A. vera* and others. They are used for dyeing glove-leathers.

FIG. 71.—Babool (*Acacia arabica*).

A. nilitica, Egypt. Pods called *neb-neb* or *bablah*.

A. catechu, India. The wood yields cutch or " dark catechu." A lighter coloured variety called *kath*, containing much crystallised catechin, is also made in India, and principally used for chewing with betel. *A. catechu* is a tree 30 to 40 feet high, common in India and Burmah, and also in tropical East Africa, where, however, it is not utilised. In Southern India, *A. suma* is also used for the same purpose.

Trees of about 1 foot diameter are cut down, and the wood (some state the heart-wood only) is reduced to chips, and boiled with water in earthen jars over a mud-fireplace. As the liquor becomes thick and strong it is decanted into another vessel, and the evaporation continued till the extract will set on cooling, when it is poured into moulds made of leaves or clay, the drying being completed by exposure to the sun and air. "Kath," or pale cutch, is made in Northern India by stopping the evaporation at an earlier point, and allowing the liquor to cool and crystallise over twigs and leaves thrown into pots for the purpose. It contains a large proportion of catechin, apparently identical with that of gambier, but its tannin is much redder. Good cutch contains about 60 per cent. tanning matter, but is principally used for dyeing browns and blacks with chrome and iron mordants. It contains quercetin, a yellow colouring matter (p. 298).

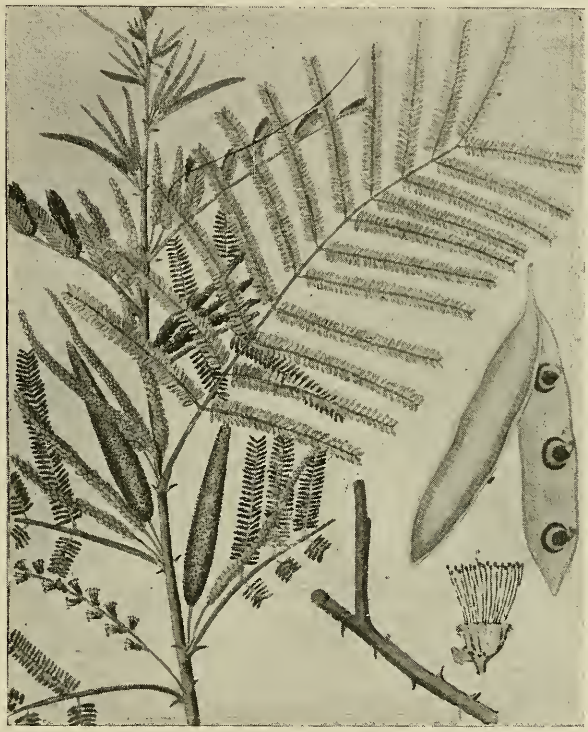


FIG. 72.—Cutch Tree (*Acacia catechu*).

A. leucophlea, India and Java "*Pilang*." Pods and bark equal to *A. arabica*.

Australia abounds in acacias (mimosas), many of which are used in tanning, but vary greatly in strength, not only according to species, but probably also by situation and growth. Probably the best information is to be found in a pamphlet on *Wattles and Wattle-Bark*, by J. H. Maiden, F.L.S., published by the Department of Public Instruction at Sydney, 1890. His analyses were made by the Löwenthal process, and can only be roughly compared with those by the hide-powder method. The analyses given are by the I.A.L.T.C. method, and mostly on samples furnished by Mr Maiden.

A peculiarity largely developed in the mimosa family is the tendency for the true leaves to be suppressed, and their place taken by the flattened and expanded midrib (phyllode). Thus leaves of two very distinct forms are common in the genus, and some acacias, as *A. heterophylla*, may have both forms on the same branch. Compare *A. pycnantha* and *A. decurrens*.

The Australian mimosas have been naturalised in India, and grow freely in the Nilgiri Hills, but the bark does not appear to be utilised.

The most important species are as follows :—

A. pycnantha (fig. 73). "Broad-leaved" or "Golden Wattle," South Australia. One of the strongest tanning barks known. A sample marked "special," analysed in the Yorkshire College, contained 50 per cent. of tannin ; another sample marked "ordinary" contained 40 per cent.

A. longifolia, the Golden Wattle of New South Wales, only contains half as much tannin as *A. pycnantha*.

A. mollissima, with its two varieties *A. decurrens* (fig. 74) and *A. dealbata*, are among the most important of the Wattle family commercially. Two samples of the former marked "Green Wattle" showed 36 to 39 per cent. of tanning matter ; another sample marked "Sydney Green Wattle" contained 41 per cent. A sample of *A. decurrens*, the second variety, was much weaker, showing only 12 per cent. on analysis.

A. penninervis (Hickory bark) is said to be particularly hardy, but its strength seems to vary. A sample from Bateman's Bay contained 38 per cent. of tanning matter.

A. binervata, another "Black Wattle," contains up to 30 per cent. tanning matter, as does also the "Weeping Willow," *A. saligna*. The latter is poisonous, and is said to be used for killing fish.

A. prominens, the bark of which resembles that of the Golden Wattle, *A. longifolia*, in appearance contains only 14 per cent. tannin.

The cultivation of wattles in Australia has been somewhat neglected, but would render possible the utilisation of many acres of land lying waste, or which have already been exhausted and rendered unfit for the growth of cereals. It requires so little attention as to make it very profitable, and wattle-growing and sheep-grazing can be combined satisfactorily after the first year, when the young trees in the plantation have reached the height of 3 to 4 feet. In Natal the Australian wattles, especially *A. mollissima,* have been acclimatised and cultivated with success, and large quantities of excellent bark are now exported to England. African wattle-barks usually contain about 30 per cent. of tannin.

Fig. 73.—Broad-leaved Wattle (*Acacia pycnantha*).

Fig. 74.—Green Wattle (*Acacia decurrens*).

Wattles grow in almost any soil, even the poorest, but their growth is most rapid on loose, sandy patches, or where the surface has been broken for agricultural purposes. When the soil is hard and firm, plough-furrows should be made at a regular distance of 6 to 8 feet apart, and the seeds dropped into these. The seed should be sown in May, having been previously soaked in hot water, a little below boiling temperature, in which they may be allowed to remain for a few hours. It should be dropped at an average distance of 1 foot apart along the furrow, in which case about 7200 seeds would suffice for one acre of land. The seed should not be covered with more than about ¼ inch of soil.

On loose sandy soil it might even be unnecessary to break up the ground in any way; the furrows may be dispensed with, and the seed sown broadcast after the land has been harrowed. After the plants have come up, they should be thinned so that they stand 6 to 8 feet apart. When the young trees have attained the height of 3 to 4 feet the lower branches should be pruned off, and every effort afterwards made to keep the stem straight and clear, in order to facilitate the stripping, and induce an increased yield of bark. It is advisable that the black and broad-leaved kinds should be grown separately, as the black wattle, being of much larger and quicker growth, would oppress the slower-growing broad-leaved one. Care should be taken to replace every tree stripped by re-sowing, in order that there should be as little variation in the yield as possible. In Victoria, the months of September to December are those in which the sap rises without intermission and the bark is charged with tannin. Analysis proves that the bark from trees growing on limestone is greatly inferior in tannin to that obtained from other formations, differing 10 to 25 per cent.

The following are South American mimosas:—

A. cavenia, Espinillo. Bark contains 6 per cent., pods 18 to 21 per cent. or more of tannin.

A. cebil, Red Cebil. Bark contains 10 to 15 per cent., leaves 6 to 7 per cent. tannin. Argentine Republic.

A. Guarensis, Algarobilla of Argentine Republic. Bark, pods, and flowers said to be used for tanning.

A. timbo or *Piptadenia*. Buenos Ayres.

A. curupi, Curupy bark. Wichmann found 18·3 per cent. tannin.

A. angico, or *Piptadenia macrocarpa* (or *rigida*), Brazil, yields "angica bark," a sample of which contained 20 per cent. of tanning matter when analysed in the Author's laboratory. Said to contain 20 to 25 per cent.

"White Bark," South America, probably an acacia; bark internally very similar to angica, if not identical.

A. horrida, "*Doornbosch*," Cape of Good Hope, bark contains 8 per cent. of tannin.

The following are other leguminous plants containing tannin:—

Inga affinis, D.C. Bark 25·8 per cent. tannin. Paraguay.

Inga feuillei, "*Paypay*," Peru. Pods said to contain 12 to 15 per cent. of tannin (doubtful). Several other species of *Inga* known to contain tannin.

Elephantorrhiza Burchellii, Elandsboschjes, Tugwar, or *Tulwah,* South Africa ; a papilionaceous plant. The air-dry root contains 12 per cent. of tannin and a great deal of red colouring matter. The roots are several feet long and about 2 inches in diameter, growing by the sides of rivers.

Acacia or *Albizzia granulosa.* New Caledonia. Fine timber tree like walnut ; bark contains 12 per cent. tannin.

Stryphnodendron barbatimao, Brazil, "barbatimao" bark. Paessler found 18 to 27 per cent. tannin.

Pithecolobium dulce. Mexico, Philippines, Malay Archipelago. Bark said to contain 25 per cent. tannin. Mexican name "camanchile." Other *Pithecolobia* contain tannin.

P. gummifera, Brazil, "Arnhatico di Campo."

Xylia dolabriformis (Benth.). An extract has been made from the wood sawdust. The yield was small, but the dry extract is said to have contained 85 per cent. tannin.

Enterolobium timbouva (Mart.), "timbo" bark. Paraguay. Bark 22·3 per cent. tannin.

E. monjolo, Brazil, "Monjolo branco de Espinho." Used extensively.

Bauhinia vahlii. (Mahurain.) Creeper growing in C. India. Cementing matter between fibres contains tannin and can be "combed" out. Fibre useful for rope-making. Tannin gives cream-coloured smooth-grained leather, but does not penetrate rapidly. Liquors have good swelling power.

GUTTIFERÆ

Garcinia mangostana. India. The rind of the mangosteen fruit contains much tannin.

Rheedia Braziliensis, Paraguay, "Pakuri." Bark 21·6 per cent. tannin and little colour.

DIPTEROCARPACEÆ

Shorea robusta. (Sal-bark.) India. Analyses by Brumwell show 6·2 to 15 per cent. tannin, which is found in the dust after disintegration ; fibre remaining contains not more than 3 per cent. tannin. It is a valuable material, giving a pale, tough leather, when used in mixture with gothar and karunda.

Vateria Indica (L.). India. Fruit contains 25 per cent. of a pale tannin.

Dipterocarpus tuberculata. India. An extract has been made, but much of the tannin became insoluble in the process.

LYTHRACEÆ

Woodfordia floribunda. (Itcha, Thawai). India. Bark and leaves contain tannin. Former used for sole leather ; gives good colour ; but cracky grain when used alone. Leaves contain 15·4 per cent. tannin and 17·2 per cent. non-tannin ; bark, 26·6 per cent. and 13 per cent. (Brumwell).

The following the writer has not been able to place botanically:—

Eucoupia cordifolia, Santiago, Ulmo bark. A considerable quantity was imported into Germany, probably for extract-making.

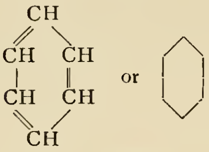
CHAPTER XIX

THE CHEMISTRY OF THE TANNINS

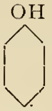
The essential constituents of tanning materials are members of a large group of organic compounds known as "tannins" or "tannic acids," which are widely distributed throughout the vegetable kingdom, and said to have at least one representative among animals, in the body of the corn-weevil. Their use in vegetable physiology is as yet uncertain, and indeed they appear in some cases to be waste products of organic change. The tannins, though varying considerably in their chemical constitution, are all marked by the power of precipitating gelatin and other proteins from solution, of converting animal skin into imputrescible leather, and of forming dark-coloured compounds with ferric salts, which are often used as inks. They are also precipitated by lead and copper acetates, stannous chloride, etc., and form insoluble compounds with many organic bases, particularly the alkaloids such as quinine and strychnine, and with basic aniline colours. They have a feebly acid character. Finally what is perhaps the most important fact must be mentioned, namely, that they are in aqueous solution negatively charged colloids.

With regard to less characteristic properties it may be said that tannins are all soluble in water, but like other colloids have no definite solubilities. They are also soluble, in part at least, in alcohol, ethyl and amyl acetates, aqueous ether, acetone, etc., but not soluble in the fat solvents, including dry ether. Since tannins are uncrystallisable and without definite melting points, their preparation in a state of purity is a matter of the greatest difficulty. Indeed gallotannin is perhaps the only member of the class that has been prepared pure. Methods used for other tannins are very empirical and tedious, and their description is outside the scope of a general account.

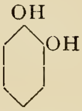
A classification of tannins according to chemical constitution is difficult, since so little is known of them in this respect. Perhaps the most useful classification is the early one based on the colour reaction with ferric salts, *i.e.* the division into the two classes: pyrogallol (iron-blueing) and catechol (iron-greening) tannins. It has been found that tannins giving a blue colour with ferric salts yield pyrogallol on dry distillation or sodium gallate on fusion with alkali, whilst those giving a green colour yield catechol or the sodium salt of protocatechuic acid. These bodies are phenols or phenolic acids. The phenols are a class of derivatives of benzene C_6H_6, in which one or more of the hydrogen atoms are replaced by hydroxyl (—OH) groups. Common phenol or carbolic acid is the simplest representative:



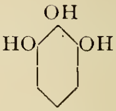
Benzene.



Phenol.

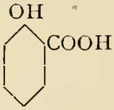


Catechol.

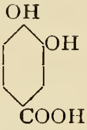


Pyrogallol.

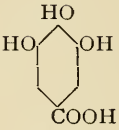
In the phenolic acids a further hydrogen atom in the ring or nucleus is replaced by the carboxyl (—COOH) group, and thus a true acid is formed:



Salicylic acid.



Protocatechuic acid.



Gallic acid.

How these bodies are linked together in the tannin molecule is not known with certainty except in the case of gallotannin, nor how they are combined with glucose, as often appears to be the case. A. G. Perkin suggests the subdivision of the pyrogallol class into two others, namely, gallotannins and ellagitannins, or, better, into "depside" tannins and ellagitannins. The last-named class contains an ellagic acid nucleus, and yields this acid ("bloom") on fermentation, or hydrolysis with mineral acid. This treatment with gallotannins gives rise to gallic acid. From the point of view of leather technology, however, this further classification is of little moment, as it almost amounts to providing a separate class for gallotannin.

The two classes, pyrogallol and catechol tannins, are fairly clearly distinguishable by other reactions. Boiling with dilute sulphuric acid gives a precipitate of "reds" or phlobaphenes with catechol tannins. The behaviour of the pyrogallol group has been mentioned above. Bromine water added till the solution smells strongly of it gives a yellow or brown, occasionally crystalline, precipitate with catechol tannins only. Another reaction which is generally characteristic of catechol tannins is that if concentrated sulphuric acid is added to a single drop of infusion in a test-tube a dark red or crimson ring is formed at the junction of the two fluids, and on dilution with water the colour is generally pink. Pyrogallol tannins, on the other hand, give a yellow or brown ring, which dilutes to a yellow solution. This reaction is of great delicacy. The formaldehyde test, due to Stiasny, gives another means of distinction. Catechol tannins when boiled with formaldehyde and hydrochloric acid are completely precipitated, pyrogallol tannins incompletely or not at all. The precipitate obtained by adding lead acetate to a tannin solution is soluble in acetic acid in the case of catechol tannins, partially at most in the case of pyrogallol tannins. Finally it may be mentioned that the catechol tannins contain as a rule about 60 per cent. of carbon, those of the pyrogallol group only about 52 per cent.

The differences mentioned above hold generally, but not without exception. An important case is that of oak-bark, which contains both types of tannin. This may be the reason why no material can be so satisfactorily used alone as oak-bark.

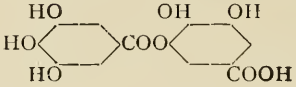
The commoner tanning materials fall into the two classes described as follows :—

Pyrogallol tans : Gallotannin, sumach, oakwood, chestnut, myrobalans, valonia, divi-divi, algarobilla.

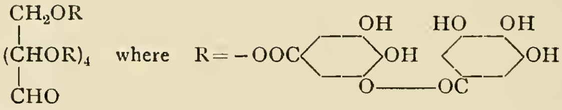
Catechol tans : Pine barks (including hemlock), larch, acacias and mimosas, quebracho, mangrove, canaigre, and gambier.

The tannin of oak-bark appears to be principally catechol tannin.

In the case of only one tannin, gallotannin, can it be said that the chemical constitution is known. Other tannins have been investigated, but without much success ; certain chemical groups have been recognised in them and so forth, but little fundamental knowledge has been gained. The case of gallotannin, however, is interesting and merits some remark, since it has been worked upon since the time of Liebig, but has only very recently (1919) been finally settled. The empirical composition of supposedly pure specimens agreed closely with the formula $C_{14}H_{10}O_9$, and on hydrolysis the principal product was gallic acid. Many workers, however, found glucose on hydrolysis, and much discussion centred on the question as to whether this glucose was part of the tannin molecule or simply an associated impurity. Gradually the latter view prevailed, and for many years the view of Schiff was adopted, namely, that gallotannin was *m*-digallic acid:

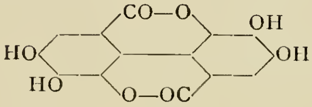


There were difficulties, however, in this view, even though practically all of the reactions of tannin could be explained by it. In the first place, the molecular weight determinations carried out on tannin, though in very poor agreement, were without exception very much higher than that of a digallic acid. Secondly, tannin is always optically active; there should be therefore at least one asymmetric carbon atom in the molecule, *i.e.* a carbon atom with each of its four bonds attached to different atoms or groups. This is not provided for in Schiff's formula. Another difficulty was that glucose was summarily ruled out as a constituent of the molecule. The subsequent work of Fischer and his collaborators has led to a much more satisfactory formula. At the outset they adopted a method of purification previously used by Perkin and Stiasny which implied a disbelief in the presence of a carboxyl group. This method was to neutralise a tannin solution to litmus with dilute alkali and extract the tannin with a solvent. This was to leave behind gallic acid as sodium salt, but would obviously do the same with any digallic acid present. Phenols, other than phenolic acids, would not be neutralised under the circumstances. Tannin thus purified was found to yield 7 to 8 per cent. of glucose on hydrolysis. The details of Fischer's subsequent work are too complex for description here. He had, however, before 1913, brought forward the strongest evidence that gallotannin was an ester of one molecule of glucose and five molecules of digallic acid, *i.e.* penta-digalloyl-glucose:

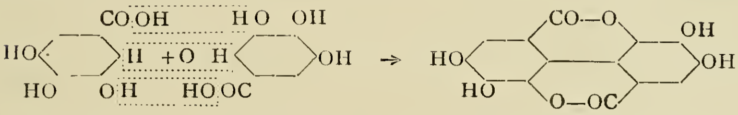


The synthesis of this body in the laboratory was hindered by many difficulties, but finally Fischer prepared a substance identical with the tannin of Chinese galls save in one respect, the specific optical rotation in aqueous solution. In organic solvents the optical activity presents no difficulty. There can be no reasonable doubt that Fischer has produced at least an isomer of natural tannin. Dr Freudenberg, who was associated with Fischer in much of this work, is continuing investigations on tannins, particularly chebulinic acid from myrobalans and hamameli tannin from *Hamamelis virginiana.* This latter body is exceptional in being crystalline.

It has been mentioned above that solutions of pyrogallol tannins deposit " bloom " on standing. This is particularly the case with valonia, divi-divi, and myrobalans. A similar precipitate is obtained on boiling with dilute acid, especially in the presence of an oxidising agent such as hydrogen peroxide. " Bloom " is ellagic acid, and has been shown to have the constitution



Possibly the ellagic acid is formed as follows : hydrolysis of the tannin, either by fermentation or the action of acid, results in the formation of gallic acid ; two molecules of gallic acid then unite, partly by oxidation and partly by loss of water, to form ellagic acid :



To understand the above it must be remembered that at the corners of the hexagon representing benzene a $\equiv CH$ group is always present except when a substituting group has been introduced ; such a group replaces the H of the $\equiv CH$ group. Two hydrogen atoms have been written in the left-hand side of the equation to indicate where the oxidation takes place.

Numerous methods have been devised for the synthesis of ellagic acid, but they can all be represented by the equation given, since they only differ with regard to the particular oxidising agent used. Löwe oxidised gallic acid with arsenic acid, Ernst and Zwenger boiled ethyl gallate with sodium carbonate solution in presence of air, Griessmayer oxidised with water and iodine ; the best methods are those of Perkin, in which potassium persulphate and acid are used, and of Rupe, in which acid and sodium nitrite are used.

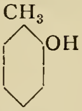
Prepared synthetically or otherwise, ellagic acid is a more or less yellow, sandy, or crystalline substance of remarkable stability. It does not melt below 360° C., but sublimes with considerable decomposition at higher temperatures. Its almost complete insolubility in the usual organic solvents was a great obstacle to its purification until Perkin found that it dissolved easily in pyridine, from which it could be crystallised in prismatic needles. These crystals contain pyridine, which may be removed by washing with alcohol and drying at 160° C. Ellagic acid may perhaps dissolve in other basic liquids such as quinoline or solutions of urea. Solutions of ellagic acid in alkali are yellow, and give a crystalline precipitate when diluted with hot alcohol and acidified. The most important colour test for ellagic acid is Griessmayer's test, carried out by adding nitric acid containing nitrous acid and subsequently diluting. A blood-red coloration is given, once thought characteristic of ellagic acid, but shown by Perkin to be also given by an allied substance, flavellagic acid, which contains five hydroxyl groups.

Leather tanned with bloom-yielding materials naturally contains ellagic acid, the presence of which is often desired, as it gives some weight and solidity to the product. In order to extract it the leather should be thoroughly freed from fats and water-soluble matter in the usual way, the residue then well dried, and finally extracted with hot pyridine. Ellagic acid so obtained was found by Nierenstein to be identical with the synthetical product.

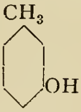
Most solutions of catechol tannins are decomposed by long boiling, particularly with acids, or by heating under pressure. A reddish precipitate is obtained totally different from bloom, and to which the name of " phlobaphenes " or " reds " is usually given. These phlobaphenes appear to be present to some extent ready formed in the solutions capable of yielding them. If alcoholic or very concentrated aqueous tannin extracts are poured into cold water a red precipitate is sometimes formed which will not redissolve. Phlobaphenes appear to be produced from the catechol tannins by condensation of molecules through anhydrisation or oxidation, or both. Nothing exact can, however, be said on this point, since the constitutions of catechol tannins and phlobaphenes are alike unknown. Alcohol, dilute alkalies, sulphites, and borax dissolve phlobaphenes, and attempts have been made on these lines to render phlobaphenes available for tanning. One of the most successful of these efforts has been the sulphiting process of Lepetit, Dollfus, and Gausser, who heat with bisulphite under pressure. Some phlobaphenes are insoluble in water even at boiling temperatures, though they dissolve to some extent in the presence of sugars, tannins, etc. This is probably a case of the well-known colloidal phenomenon of peptisation. Other phlobaphenes are more soluble in water, probably because they are more hydrated. Such substances are able to precipitate gelatin and combine with hide, and must be regarded as difficultly soluble tannins. It is on this account that the determination of insoluble matter in tanning extracts becomes so difficult to decide upon. A sharp distinction between difficultly soluble tannin, and strictly insoluble and consequently useless matter, cannot be drawn.

This chapter could not be concluded without some mention of the artificial tanning materials of the Neradol class. Many of these are on the market and in wide use. The actual details of preparation are largely manufacturers' secrets in the case of both Continental and British products, but the principle underlying their preparation is generally the same. It has long been known that phenol-sulphonic acids would condense with formaldehyde, or other aldehydes, in the presence of acids to form complex bodies of higher molecular weight. These bodies are usually capable of tanning, but owing to their insolubility in water are of no practical use. Stiasny's important discovery was that by a suitable process water-soluble tanning substances could be prepared. For example, 10 kilos. of phenol is heated at 105° to 106° C. with its own weight of concentrated sulphuric acid for two hours. The mixture is then cooled to 35° C., and about 4½ kilos. of 30 per cent. formaldehyde gradually added over a period of three hours without allowing the temperature to rise. This latter precaution is absolutely essential, and is to avoid the production of insoluble bodies. After the formaldehyde has been added the mixture is stirred for a few hours. Thus one obtains about 24 kilos. of the crude condensation product. In practice phenol is not used, but is replaced by the cheaper commercial cresylic acid, a mixture of the three isomeric cresols:

Phenol.



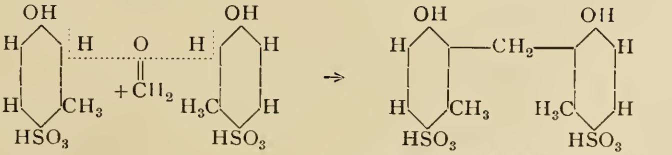
o-cresol.



m-cresol.

p-cresol.

The formation of Neradol D may be formulated as follows, according to Grasser:



Dicresylmethanedisulphonic acid.
Neradol D.

Neradol N and Neradol ND are similar products prepared from naphthalene sulphonic acids ; Ordoval G is prepared from higher hydrocarbons, principally retene. All these bodies must be neutralised to a suitable degree with alkali before they are ready for use.

Neradol D is a substance of brown colour similar in appearance to ordinary tanning extracts, and has a characteristic smell of phenol. It is completely soluble in water, and the organic part, but not the sodium salts produced by neutralisation, in alcohol and in ether. The ordinary fat solvents, with the exception of ether, exert no solvent action. The aqueous solution is usually acid to methyl orange, and gives, according to Grasser, the following reactions : with barium chloride, a white precipitate insoluble in nitric acid ; a deep blue colour with ferric salts ; no precipitate with bromine, or with formaldehyde and hydrochloric acid ; complete precipitation with gelatin ; a distinct precipitate with aniline and hydrochloric acid. Its behaviour is thus very much like that of a pyrogallol tannin. It will be noticed that it behaves with regard to aniline in the same way as sulphite-cellulose extract. Neradol D in acid aqueous solution is electrically negatively charged. The practical use of Neradol D cannot be described here, but attention may be drawn to its power of solubilising phlobaphenes, and its probably consequent property of lightening the colour of leather tanned with quebracho and similar materials.

The reactions of Neradol N and Ordoval G are summarised in the following table, due to Grasser:

	Neradol N.	Ordoval G.
Gelatin . . .	Ppt., somewhat soluble in excess of tannin.	Moderate pptn. in fine flocks.
Ferric chloride .	No colour.	Slight darkening.
Barium chloride .	White ppt., insoluble in HNO_3.	Turbidity.
Bromine water .	No reaction.	No reaction.
Silver nitrate . .	No reaction.	Opalescence.
Aniline and HCl .	Ppt., soluble on heating.	Brownish-black ppt.
Formaldehyde and HCl . . .	..	No. ppt.

The failure of the iron reaction is probably due to the absence of hydroxyl groups.

CHAPTER XX

THE SAMPLING AND ANALYSIS OF TANNING MATERIALS

ALTHOUGH the analysis of tanning materials falls more properly within the scope of a book for chemists than one intended primarily for tanners, and though it has been treated at considerable length in the *Leather Industries Laboratory Book* and, more recently, in *Leather Chemists' Pocket Book*,[1] a slight sketch must now be given of the methods in general use, since it is of great importance that at least the principles on which they are based should be understood by all to whom they are of practical interest; but the method has become too complex and detailed to be within the scope of the ordinary tanner, and those who wish to pursue it will find full details in the books quoted, and in the Journals of the respective Associations, of which it is open to anyone to become an Associate who is interested.

It must specially be insisted on, that absolute adherence in every detail to the methods given is essential to obtaining concordant results, and little points of manipulation which appear in themselves unimportant are frequently the result of long experience and careful discussion. The members of the Society of Leather Trades' Chemists especially are bound by their rules to make note in their analytical reports of any deviation, however small, from the prescribed process.

The first step in the analysis of any material is to draw a sample truly representing the bulk, which usually depends on the tanner himself or his agent, and which is often by no means easy, while failure to accomplish it is probably the cause of more errors and disputes than any inaccuracy of the method of analysis itself. In very many cases chemists are blamed for discrepancies which really exist in the samples supplied to them, and they can only hold themselves responsible for the accuracy of their analyses when the sampling has been done strictly according to the rules prescribed by their Associations. On this account, all important samples should be drawn in the presence of a principal or some other responsible person.

In liquid extracts, the thorough mixing of the liquid is of the greatest importance. Most extracts contain a portion of " diffi-

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[1] E. & F. N. Spon, 1919.

cultly soluble" tannins (see p. 351), which slowly settle to the bottom or adhere to the sides of the cask, from which such expedients as merely rolling a full cask are quite inefficient to dislodge them. In fact nothing but taking the heads out of a sufficient number of casks, and actually stirring them with a suitable plunger, which should be specially applied to the sides and bottom, or emptying the entire contents of the casks into a tank in which the whole can be adequately mixed, is really thoroughly reliable, though at times it is necessary to be content with less satisfactory methods. In any case, when it is probable that samples must be submitted to more than one chemist, the whole should be drawn at once, thoroughly mixed and divided, and sealed in separate bottles, and in dividing a sample the same care must be taken to ensure complete mixture as in drawing the original sample.

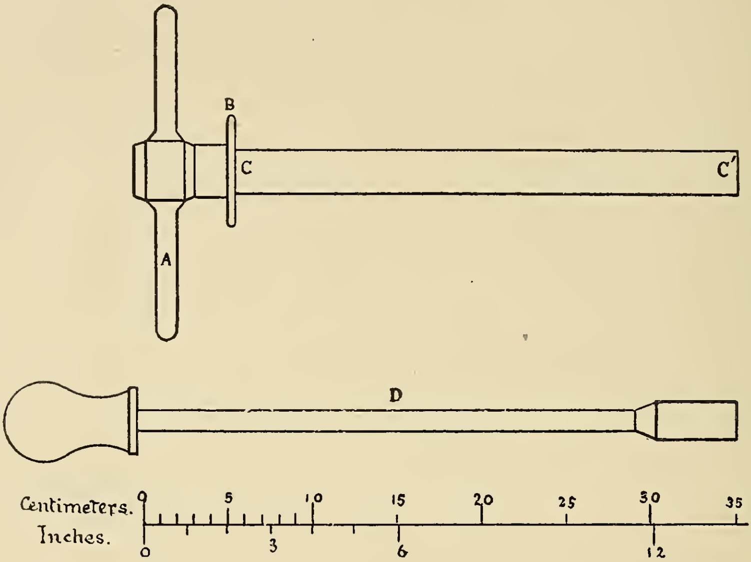

Fig. 75.—Kathreiner's Sampling Tools. A, strong cross-handle; B, guard-disc; C C′, brass tube sharpened at C′; D, brass or wooden plunger.

Solid and pasty extracts, such as quebracho, cutch, and gambier, are still more difficult to sample fairly, as the outside is almost invariably much drier than the interior. Generally the only way is to select such portions as are thought fairly to represent the bulk, to chop them into moderately small pieces, mix and seal in an air-tight tin, leaving it to the chemist to draw from these the smaller sample required for analysis. Gambier is best sampled with a tubular tool like a cork-borer, designed by Mr Kathreiner (fig. 75), which must be passed completely through the bale, or the cylindrical sample of gambier cannot be withdrawn. The same tool may also be used for sampling sumach in bags if the damage to the bag is not objected to. If such a tool is not available, the only fair way to sample gambier is to cut slices completely through the bale with a clean fleshing-knife. In any case it is of the utmost importance that the sample once drawn should be mixed as rapidly as possible, and at once enclosed in an *air-tight* box or jar, sealed, and labelled.

Dry tanning materials, such as bark and valonia, require judgment in selecting samples which fairly represent bulk. If they are of a nature which do not really separate into dust and fibre, a good method is to grind a sufficient quantity in an ordinary bark-mill, and, after well mixing, to draw the sample from the ground portion. In other cases it is best to empty a sufficient number of bags one upon another in layers on a smooth floor, and to divide by "quartering"; that is, by halving the total quantity down to the floor, and halving the half again till the part is reduced to a suitable sample. In such materials as valonia and divi-divi, the dust or beard is usually much stronger than the average of the pods or cups.

The same sort of precautions are required in drawing the still smaller sample required for analysis from the larger original sample, but these are sufficiently detailed in the directions of the chemical text-books. As materials usually require finer grinding than can be managed with the mills employed in the tannery, a suitable mill may be provided, and one of the simplest, at a moderate price, is the No. 4 drug-mill made by A. Kenrick & Sons, Limited, West Bromwich (fig. 76), but this, and the final drawing of a small sample for analysis, is usually left to the chemist. Coffee mills are seldom strong enough for the purpose, but if nothing better is available, the sample must be *thoroughly* dried before grinding, and its loss of weight noted and taken into account in calculating the analysis, care being taken that the sample after grinding is so preserved that it cannot re-absorb moisture. Valonia, myrobalans, and even barks, may before grinding be broken with a flat-faced hammer on a thick cast-iron plate, with raised edges to prevent loss from flying fragments. Barks in "long rind" may be bound in bundles with wire and sawn into short lengths, or the sawdust taken for analysis.

As to the analytical process itself, almost innumerable methods have been proposed. Dekker in his book on *Die Gerbstoffe* describes more than eighty, but of these only two have kept their place as of practical value—the "hide-powder" method for all commercial analyses, and the Löwenthal volumetric method for some purposes of tannery control. The earliest attempt at quantitative analysis of tanning materials seems to have been made by Biggin in 1800, and improved by Davy in 1803 or 1804. The tanning infusion was precipitated with gelatin, and the precipitate dried and weighed after more or less washing, and the tannin reckoned as half the weight of the precipitate. Complete washing was difficult or impossible, and it was found that different proportions of tannin were carried down in the precipitate by different concentrations of the solutions. Almost innumerable metallic salts will precipitate tannin, especially those of the heavy metals, and many methods have been founded on this fact, but the precipitates are of inconstant composition, and as the tannins are a class, differing rather widely in chemical constitution, and not a single chemical individual, as was at one time supposed, it follows that even if an actual tannin-salt could be obtained, it would be of different proportions for different tannins. In fact several of the methods with metallic salts will give fair results if only one species of tannin is to be determined. A more serious trouble perhaps is that all natural tanning materials

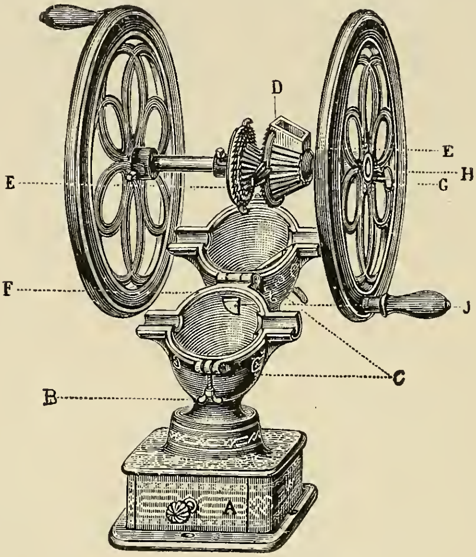

Fig. 76.—Kenrick's Drug-mill.

contain not merely the tannins themselves, but their phenolic derivatives, such as gallic acid, which are incapable of tanning, but which are mostly precipitated by the metallic salts. The necessity therefore arises of removing these bodies by a separate operation, which is not generally possible.

Much more useful and rapid methods are those dependent on the oxidation of the tannin by a volumetric solution of potassium permanganate or some other oxidising agent, and the best of these still seems to be the original Löwenthal method invented in 1860, and subsequently improved by Löwenthal and others. This depends on the oxidation of the tannin in very weak solution in presence of a known quantity of sulphindigotic acid till the deep blue of the solution is changed to a clear yellow. The sulphindigotic acid serves not only as an indicator, but as a regulator of the oxidation, only those substances being attacked which are more readily oxidisable than the indigo itself. As, however, these include gallic acid and other phenolic derivatives generally present, it is necessary to remove the tannin by hide-powder, or by precipitation with gelatin, and make a second determination of the remaining "non-tannins" and thus obtain the permanganate-value of the tannin by difference, that of the indigo being deducted in each case. The process sounds complicated, but where a number of determinations are to be made it is the quickest known, as each titration only takes a few minutes, and the end-point is quite sharp, while the removal of the tannin, especially with a gelatin solution in presence of salt and sulphuric acid, is also very rapid. It has the advantage that it can be done in extremely dilute solution and is thus especially adapted to the control of weak liquors but, like all other purely chemical methods, it gives different results with different tannins. The permanganate-value of the different tannins may be determined by comparison with the hide-powder gravimetric process, and the permanganate solution is now generally standardised by a comparison with a solution of pure gallic acid under the same conditions as the tannin test; but the chief use of the method is for the relative determination of a series of liquors made from the same materials, as in the control of suspender liquors, or of the exhaustion of spent tanning materials. Full details of the precautions required in its execution may be obtained from the text-books already named, and if the standard solutions are provided, it should not be beyond the ability of an intelligent foreman to carry out the actual determinations for the purposes just suggested.

The hide-powder gravimetric process is of a quite different character, and is really of the nature of a miniature tannage carried out on a laboratory scale and in a very limited time. It is therefore applicable to all tannins, and determines the actual quantity of matter present which is absorbable by hide, but of course does not give the relative value as affected by colour or by the quality of the leather produced. Being an empirical process, it is necessary to carry out the experiments with absolute uniformity to ensure comparable results, and though it has now been perfected so that very concordant results are obtained, there are still several sources of error which have not been completely eliminated, one of which is the difference of absorptive power of different batches of hide-powder, even when the greatest care is taken to ensure a uniform product. For this reason the powder of a single maker is employed by all the chemists of the Society, and no batch is allowed to come into use till it has been practically tested and passed by a committee appointed for the purpose.

The principle of the method is that a weak solution is made from a known weight of the tanning material in a given volume of water, and, after filtration, the dissolved matter it contains is determined by evaporating 50 c.c. of it to dryness and weighing in a tared basin. As this includes all soluble matters present, it is necessary to remove the tannin from a portion of the solution by shaking with a known weight of a carefully washed and lightly chromed hide-powder, which can be proved to give no appreciable soluble matter when shaken with pure water, and to determine the " non-tannins " by evaporation of a second 50 c.c. under similar conditions. The " moisture " in the original sample is now determined by drying a weighed portion (generally at 100° C. *in vacuo*), or alternatively, in the case of extracts, the " total solid matter," by evaporating 50 c.c. of the well-mixed *unfiltered* solution ; and from these *data* the following results are obtained by calculation:—

" Tanning matters absorbed by hide " (=total soluble less " non-tannins ").

" Non-tannins " (by direct weighing of the dried detannised solution).

" Moisture " (by loss on drying the original substance, or by deduction of total solids from total weight used, or from 100 per cent.).

" Insolubles " (by deduction of the above from 100 per cent.).

It is curious that the greatest discrepancies between different analysts have often occurred in those points which seem most easy of direct determination, such as the amount of moisture present in the original sample. This may be partly accounted for by the difficulty of preserving a sample without loss or gain of moisture, but it also shows the necessity of absolute uniformity in the temperature of drying, the degree of vacuum used, and all other conditions which may affect the result.

As has been observed, the amount of " non-tannins " found is varied to a certain extent by the character of the hide-powder, although the tanning matters are always completely absorbed, as is shown by the detannised liquor failing to give any cloudiness with a solution of slightly acidified and salted gelatin. The fact is that a proportion, sometimes considerable, of the phenolic non-tannin derivatives, which are always present in tanning materials, are absorbed by the hide-powder, though the greatest care has been devoted to reducing this to the smallest possible. These non-tannins are also absorbed by hides in the actual tanning process, so that they are not commercially valueless to the tanner, but they are only loosely combined, and can be removed by sufficient washing, so that, scientifically, they should not be regarded as tanning matters. J. A. Wilson has recently attempted to overcome this error by washing the hide-powder after use in detannising, and so obtaining what he calls " the true tanning value," and this often differs to an unexpected degree from the results of the official method. This will be discussed in detail on a later page. In any case it is desirable to approximate the results of analysis as much as possible to the scientific standard, and there is no doubt that further efforts will be made in this direction, but, in the meantime, the results of the official method have become of great commercial importance, and changes cannot be rashly made.

A further point on which the present method is unsatisfactory, but to which the same remarks apply, is that of the estimation of so-called " insolubles " in extract. The greater part of this is not really insoluble or useless to the tanner, but consists of difficultly soluble tannins which separate from the hot solution as it cools in a very finely divided and colloidal state, so that it is almost impossible to remove them by filtration. When the extract is used in tanning much of this ultimately passes into solution and is absorbed by the leather, and the writer has experimentally tanned sheep-skin quite satisfactorily with the separated " insolubles " of quebracho extract by merely drumming with cold water. On filtration, the amount which passes through is not only affected by the texture of the filter, but by the exact temperature of the solution, and the length of time during which it has been cooling, and it is almost impossible for two chemists to obtain identical results, while solutions which are transparent to transmitted light may contain 10 per cent. of matter which may be removed by closer filtration. It was hoped that these difficulties would be largely overcome by the use of the Berkefeld "candle-filter," which consists of a hollow cylinder of finely divided silica cemented by some adhesive, and through which the liquid is forced by atmospheric pressure. This did not by any means wholly overcome the difficulty, and during the war it was impossible to obtain "candles" of the same constant texture, and recourse had again to be made to filter-paper with the assistance of powdered kaolin. This introduces a fresh difficulty, since some paper itself absorbs a small amount of tannin, which must be allowed for. It is now stated that satisfactory "candles" can be obtained. Really insoluble matter, such as sawdust and fragments of vegetable tissue, are rare in well-manufactured extracts, and are easily removed, while the so-called "insolubles" are mostly completely soluble at a higher temperature or by the addition of a little ether, and it has been suggested that a filtration should take place under these conditions, when in most cases no "insoluble" would be reported. As, however, many extracts are rendered wholly soluble by additions of bisulphite and in other ways, it is necessary that these should be distinguished, though perhaps a measurement or statement of the turbidity at laboratory temperature might be sufficient. Clear-soluble extracts are largely used for bleaching purposes, but as tanning agents they give porous and light-weighing leather, while the difficultly soluble tannins greatly contribute to weight and solidity.

Although for many purposes the colour of leather is quite unimportant, light colour has become a fashion with a money value; and where leather is to be dyed a clear shade, it is essential. The effect of a tanning material in this respect is best determined by tanning small pieces of prepared calf- or sheep-skin for a determined time in a solution of determined strength. Details of the execution of such experiments are given in the laboratory text-books. They do not, however, give *numerical* results which can be inserted in a contract; and neither samples of extract nor of leather can be kept unchanged for a length of time, so that a direct optical measurement of the colour of the solution, which will give definite figures, has become very customary, as although the colour of the liquid bears no very definite relation to that of the leather which will be produced, it serves as a mode of comparison of the bulk delivered with the original sample on which it was bought. The method usually adopted is to compare the colour of the filtered analytical solution in a half-inch (now 1 cm.) glass-sided cell with that of the graded glasses of the Lovibond tintometer till a match is obtained. As the analytical solution varies somewhat in strength of tannin, the result is usually calculated to that which should be given by a solution containing 0·5 per cent. of tanning matter as shown by the analysis. This method is imperfect in many respects, since the colour of the glasses, though visually the same as that of the liquor, is really differently constituted, as will be seen at once on comparing the two by a spectroscope. While the spectrum of the liquid shows a regular gradation from the blue end of the spectrum, which is most absorbed, to the red, that of the glasses is irregularly banded, especially in the green, which is specially absorbed by the red glass. If the two colours were really identical, their match would not be affected by the quality of the light, which would influence both in the same way. As it is, however, if both be looked at through a coloured glass they will usually cease to match, and similarly on a clear day with a blue sky the match will not be the same as on a dull day, or with a yellow fog, or by artificial light. It was found that even using the identical set of Lovibond glasses a different match was required in London to that obtained under the clearer sky of Paris. For the same reason a double thickness or strength of the liquid is not matched by doubling the glasses, and the calculation from the approximately 0·4 per cent. analytical solution does not give the same result as one obtained direct from a 0·5 per cent. solution specially made after the analysis is completed. A further difficulty arises from the fact that the colour of solutions usually darkens on standing. Attempts have been made to get over the differences in daylight by the use of artificial light, either of the Welsbach burner or from a tungsten or Nernst electric light, but besides the difficulty of keeping these lights really constant, there is the still more formidable one that the Lovibond glasses do not seem always to agree perfectly in different sets, although the greatest care is certainly taken to make them accurate.

It is desirable that some method should be found either to measure direct by the colours of the prismatic spectrum, or to refer to those of chemical solutions which could at any time be accurately reproduced in the laboratory, but neither is easy, and it is difficult to find a mode of statement which would be at the same time accurate and definite, and convey to tanners any clear idea of the actual colour. For the first purpose it is difficult to find three colour solutions suitable and at the same time sufficiently permanent, and for the second, in addition to the difficulty of intelligible statement, costly and very accurate apparatus would necessarily be required. A special difficulty is to find a red solution really permanent to light. Coal-tar colours are almost impossible to obtain of the requisite purity, and usually fade or change, and even cobalt chloride becomes brown on continued exposure to light. The writer has already spent much time on research to overcome these difficulties, and with considerable success, and hopes to publish details shortly. It is complicated by the fact that the colours obtained by superposing glasses are complementary to those given by direct mixture of the light of corresponding colour. Abney's small book on *Colour Measurement*,[1] or the more recent one of Luckiesh [2] on the same subject, may be referred to for further information.

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[1] Kegan Paul, Trench, Trübner & Co. (Out of print.)

[2] Luckiesh, *Colour and its Applications*. Constable.

CHAPTER XXI

PRINCIPLES OF THE VEGETABLE TANNING PROCESSES

The processes employed in the production of leather with the vegetable tanning materials vary extremely according to the class of leather which is being produced, both in the materials selected and in the time required. In sole leather tanning, where thick hides are used, and where diffusion is the only force acting to carry the tannin into the hide, many months are frequently needed, while with thin skins, and with the aid of mechanical motion, which circulates the tanning liquid between the fibres, the process is often complete within a few hours. "Drumming" or other similar mechanical means are now largely used on the heavier leathers, with great consequent shortening of the process. Differences in the strength of the liquors, according to whether hard or soft leathers are to be produced, and the mutual action of the acids naturally present in the liquors, and of the tan, have also a determining effect upon the quality of the product; and much depends on the special properties of the tanning materials selected.

The simplest form of tanning in principle is probably the old-fashioned method of sole leather manufacture. For this purpose the hides are usually "rounded" or trimmed after liming, unhairing, and fleshing, so that the most valuable part, the "butt," can be tanned separately from the "offal," which frequently gets cheaper materials and a much shorter tannage. The butts are usually washed in water to remove a portion of the lime, considerable care being required at this stage to avoid carbonation and fixation of chalk by free carbonic acid, or hydric calcium carbonate (temporary hardness) in the water employed, or by the free carbonic acid of the air. This somewhat primitive process can at best only remove a small portion of the lime, since so long as the lime remains in the caustic condition it is very obstinately held by the hide-fibre. Advanced tanners now employ weakly acid baths, in addition to washing, in order to produce more complete deliming, and this effects a very considerable improvement of colour and economy of tannin in the early liquors. The use of weak organic acids (formic, acetic, lactic, or butyric, free from iron) or of boric (boracic) acid in solution of about 4 lb. per 100 gallons, in which the butts are kept in motion, are among the safest and most satisfactory ways of removing surface-lime and improving the colour, but even the stronger mineral acids may be used successfully with caution (see Chapter XIV.). Dilute solution of sulphurous acid, made by burning brimstone (p. 24), is also very satisfactory.

Acids should never be used of such strength as to materially swell the butts, and the great advantage of the "weak acids" is that from their low ionisation they can be used more freely, while "strong" acids must be added in very small and repeated doses. For further particulars see Chapter XIV.

If hides, before bringing into the liquors, are exposed either to the carbonic acid of the air or that of "temporary" hard water a precipitate of lime carbonate is formed in the skin which is much more difficult than free lime to remove in acid deliming. A point of great importance is to keep the goods from the time of unhairing till they go into the liquors under water in which there is always a trace of caustic lime, or which at any rate are free from carbonic acid. In deliming sole leather with acids it is best to give the full dose of acid required at once, and not gradually, so that it may act most powerfully on the exterior, and remove any carbonates present, before it penetrates to and becomes neutralised by the excess of lime in the interior. This is exactly the reverse of what is advisable with dressing leather, where the object of the tanner is to remove lime as uniformly and completely as possible, without excessive acidity of any part. Of course hides should not, even in the case of sole leather, be allowed to go into the liquors while any acid swelling of the surface remains, but this will soon disappear if the goods are suspended for a time in cold water after deliming, unless excess of acid has been used (*cp.* p. 203 *et seq.*).

Whether acid be used or not, the butts are now usually suspended in deep pits containing old and nearly exhausted tan liquors. These liquors contain a certain amount of lactic and acetic acids, derived by fermentation from the sugary matters of the tanning materials, and also, in some cases, weak acids originally present in the materials themselves. The presence of these acids is most important to successful tannage, and their effect is twofold: in the first place, they neutralise and remove any lime which still remains in the butts; and, secondly, they bring the butt into a slightly acid condition, which is necessary to tannage, and in which it remains plump and swollen in the liquors, while the tannin gradually penetrates and tans the fibre. If, as frequently happens, especially in modern yards where extracts are very largely used, the natural acid of the liquors is not sufficient for this purpose, the lime combines with the tanning matters, and the butts either become discoloured at once, or darken by exposure and oxidation; when they come to be dried, while the pelt remains flat and insufficiently swollen. To avoid this trouble, resort is sometimes had to artificial acidification of the liquors. As a general rule, it may be stated that it does not answer to mix the stronger mineral acids directly with the liquors, but lactic and acetic acids may be used, or even oxalic acid may be added to the suspenders in such quantities as to precipitate and remove the lime which they contain, setting free the organic acids with which it had been combined. The use of oxalic acid should never be pushed further than this, as it has a most powerful swelling action on the hide, and goods which are too much swollen by acids tan dark and brittle. The acidity of such liquors is usually determined by Procter's lime-water test,[1] *i.e.* the volume of saturated lime-water which can be added (with constant stirring) to 10 c.c. of the clear filtered liquor without producing a permanent cloudiness. This test does not with any accuracy indicate the swelling power of the liquor, which depends mainly on its hydrion concentration (p. 103), and is much influenced by the presence of neutral salts, but it does directly give the amount of lime which can be safely carried into the liquor without the risk of producing stains. Many of the acids present in the liquors, though too "weak" to cause swelling, are still capable of dissolving lime. If lime be present beyond this point, it does not necessarily produce immediate stains, which are due to the oxidation of the tannin salts formed by exposure to the air, and if this be avoided, the lime may ultimately be got rid of in the more forward liquors, and the hides may remain of good colour ; and this was usually what was aimed at before acid-deliming was introduced. The greatest danger of stains arises when the hides are allowed to touch each other in the suspenders. In this case white patches are at first formed where the tan-liquors have not access, and these may ultimately colour properly when the hides are moved, but their edges, where there is a little tan and a great excess of lime, usually oxidise, and remain as permanently dark map-like outlines. For this reason it is most important that the hides should be freely moved for the first few hours after coming into the liquors, either by hand, or by suspending them to a mechani-

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[1] Before applying this test to liquors containing oxalates, it is necessary to remove the oxalic acid by the addition of a known volume of calcium chloride solution before filtration.

cally moved frame. If the butts are hung on sticks, these may be allowed to rest on bearers of about 2-inch by 3-inch section at the sides of the pits, with occasional crossbars to keep them parallel, and are either suspended by iron rods from beams above, or supported on rollers, which should be brass or hard wood, motion being given by an eccentric or crank with about 6 revolutions per minute, and a stroke of 6 inches or 8 inches, space for which must be allowed in the pits. The motion considerably increases the rapidity of the tanning, and renders possible a better exhaustion of the liquors, which should usually be run away after use on the green goods. The pits are best arranged in a continuous series, the top of each pit being connected by a wooden trunk with the bottom of the next weaker, all the liquors being run in at the head end, and all the green goods brought in at the other and gradually advanced.

If the goods are brought into suspenders without previous deliming, the first action which takes place is the neutralisation of the lime at the expense of the weak acids of the liquors, or, if these are not present in sufficient quantity, at that of the tannin, which forms mostly insoluble compounds with the lime, which readily oxidise, and produce dark stains if exposed to the air, though, if protected from it, they ultimately dissolve in the more acid and stronger liquors. If the goods colour quickly (with valonia, to a lemon-yellow colour), this may always be suspected. At the same time the plumpness due to the lime disappears, and the goods become soft and spongy, and, if pressed at this stage, do not readily regain their plumpness, and pressure-marks and drawn grain are apt to remain permanently. If the liquors are of proper acidity, plumpness is gradually regained by gentle acid swelling, but this should not take place before the surface is tanned and no longer susceptible to the effect of acids, or the grain will darken and be liable to crack when dry. When hides are swollen with strong acids, as is sometimes done in the States, this is always after the surface is fairly coloured, and even then a dark layer is apt to form below the grain, where the tannin has not had time to penetrate.

If new materials have to be used for making suspender-liquors, the less astringent tans, such as gambier and myrobalans, are most suitable, and the synthetic tans, such as Neradol, are now much used, as they are very light in colour, and usually rather acid. The colour which is given in the suspenders largely determines that of the finished product.

After the hides have remained from ten days to a fortnight in the suspenders, they are usually laid in pits called "handlers," which are worked in series of six, eight, or ten pits, containing the same number of packs of goods. The weakest liquor from the youngest pack is run to the suspenders daily, a new and stronger liquor is run to the pit, which now becomes the head of the series, into which the oldest and most tanned pack of butts is moved; and the next takes its place and liquor, and so on down the series, the youngest pack finally occupying the place which had previously been taken by the last but one. In this way each pack receives a change of liquor of regularly graduated strength; and during the time which it remains in the handlers, passes from a strength of perhaps 20° Bkr. (sp. gr. 1·020) to one of about 40° Bkr. (sp. gr. 1·040).[1] During this part of the process the butt is completely or nearly coloured through, and is then ready for the "layers."

In some yards suspension is continued through the handler period, and sometimes elaborate systems of overhead cranes have been fitted to move the packs from one pit to another. These no doubt save labour, but they have the disadvantage of not changing the position of the butts to each other, and it is not certain that the economy repays the much greater cost of the installation. A good method of handling is to attach cords to two corners of the butts. These must be long enough to reach the bottom of the pit, and terminate above in rings or loops which are placed over pegs at two corners of the pit. Two men pull the butts over into the next pit by these cords, while a third man puts them down evenly in the liquor with a pole. The old method of handling with sharp hooks is much slower, and requires considerable skill to avoid scratching the grain.

In the forward handlers, dustings of ground bark or other tanning material are very frequently given, not merely to keep up the strength of the liquors, but to separate the goods from each other, and the layers only differ from these in having much heavier dusting, stronger liquors, and being allowed to remain undisturbed for greater lengths of time, ranging from a week up to a month or even six weeks as the tannage progresses. The handler-liquors are principally from the old layers, though they are frequently made up with weak liquors from the leaches, and strengthened with extracts or gambier. Goods in the suspenders and handlers tan very rapidly, and require large volumes and frequent changes of weak liquors, which the layer-pits can hardly supply. A well-thought-out system of running the liquors is one of the most important things in a heavy-leather tannery,

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[1] In modern yards quite double these gravities are frequently used, the head-liquors being correspondingly stronger.

and the pumping should never be entrusted, as it often is, to an ignorant, and possibly stupid, labourer.

Very varied materials are used in the manufacture of sole leather. Oak-bark is one of the oldest, and as regards quality one of the most satisfactory, but it is costly, not only on account of its weakness in tannin but from the light weight of leather which it gives. Valonia has been one of the favourite materials, giving heavy weight and a solid leather, in which it deposits a great deal of bloom ; but its place has been largely taken by oakwood, chestnut-wood, mimosa and quebracho extracts, which save the cost of grinding and extraction of solid materials. These extracts are now very largely consumed, principally in strengthening the layer-liquors ; the great object being not only to lessen the cost in material, but to save time, and produce greater weight and firmness. The layer-liquors in some yards where extract is used reach strengths of even 120° to 150° Bkr. (sp. gr. 1·12 to 1·15), while in pure oak-bark yards it is difficult to get above 30° or 35° Bkr. ; and even these figures are only reached by repeatedly strengthening the same liquor, in which large quantities of non-tanning substances accumulate. The opinion of the most intelligent tanners is, however, that better results are attained by a regular change of liquor, even if the apparent strength is less.

When the leather has remained a sufficient time in the layers to have attained all the weight and solidity of which it is capable, it is washed up in a clear and somewhat weaker liquor, and is ready to be taken to the shed to be dried and finished. This simple method has, however, largely given place to others less defensible, partly owing to the fact that sole leather is sold by weight, and partly to the absurd demand of the shoe manufacturer for a light colour, which he proceeds to stain black, or to cover up with a " fake " ! The usual thing now is to suspend the butts before taking into the shed in a warm and very strong liquor of " bleaching extract " very heavily bisulphited. This has the property of dissolving the " reds " or phlobaphenes, to which the leather owes a good deal of its solidity as well as its colour, and replacing the weight with soluble extract, leaving the leather bright coloured, but more porous and less waterproof than before. The synthetic tannins may be used as bleaching liquors with good effect. Another modern method of weighting is to hang the generally lightly tanned and bright-coloured butts up till half dry or more, and then to drum them with undiluted extract ; and this drying and drumming is sometimes repeated. Of course this completes the tannage and makes a firm and heavy-weighing leather, but one with an inordinately large percentage of matter which can be washed out with warm water. The goods are now taken into the shed to be dried and finished.

If the proportion of free acid in the suspender liquors is as it ought to be, it is probably rather advantageous than otherwise for a little lime to remain in the interior of the hide, as it keeps the pelt in a plump condition during the first stages of colouring, quickens the penetration of the tannin, and lessens the tendency to " drawn " or wrinkled grain, which arises when the goods go into the liquors in a flat or fallen condition. The causes of drawn grain are often a little obscure. Of course that case needs no elucidation in which the hides are submitted to the tanning liquor in a creased or wrinkled condition, which is simply fixed and made permanent. This may arise either from carelessness in handling the goods before taking into the suspenders, or from the way in which they are slung to the sticks, which often draws them into long wrinkles, afterwards difficult to remove. Drawn grain in general, however, arises from the grain surface becoming tanned and fixed in area, while the substance of the hide is in a more extended condition than that which it assumes as tannage proceeds. Hides in a flat and unswollen state are thinner, the fibres are slenderer and looser than when swollen, and consequently the hide has a larger area. If, after the grain is tanned, the substance of the hide becomes contracted in the liquor, either by swelling with acids or by the direct action of the tannin on the interior fibres, the grain is certain to be shrivelled, like the skin of a dried apple. A similar effect, produced in a mechanical way, may always be noted where a hide has been coloured hanging grain side out over a pole, so that the surface is extended at the bend, on which long wrinkles are formed as soon as it is straightened.

A hide in a slightly alkaline condition colours and is penetrated by the tan more quickly than one which is acid, though actual tannage does not take place till it becomes faintly acid. Gambier gives pelt perfectly free from lime a pale buff colour, but where lime is present the colour is always reddish and much darker, and this coloration does not disappear so readily as that with valonia, so that if gambier is to be used in the first liquors, care should be taken to remove all lime from the surface. The only known tannin which gives no insoluble compound with lime is that of the babool pod (sometimes called " gambia pod "), which is frequently used in India as a bate, and which would probably prove very useful in colouring liquors (p. 329).

When sole leather first goes into liquors it is generally swollen with lime to some extent. If the liquors contain, as they usually do, sufficient free acid (acetic, lactic) in addition to the tannins, these combine with and neutralise the lime, and the pelt, without absolutely becoming flat and thin, loses its firmness, and becomes soft and spongy. This is a favourable condition for the absorption of tannin, but care should be taken not to allow the pelt to be squeezed or pressed, or water will be squeezed out, and the pelt will not easily resume its plumpness. As the tannage proceeds, both the tannin and the acid of the liquors penetrate deeper into the pelt, the former tending to contract and the latter to swell the fibres. Thus a given quantity of acid will cause the greater swelling the less tannin is present, and therefore in strong tanning liquors more acid is required. The presence of certain products of bacterial putrefaction has a great but unexplained effect in preventing hide from swelling with acids ; and in hot weather, much better swelling is obtained by sterilising and deliming the hides with carbolic acid or one of the other coal-tar products mentioned on pp. 27–29. Boric acid may also be satisfactorily used for this purpose with dressing leathers, but should not be allowed to get into sole leather liquors, as it tends to produce a soft and loose tannage, and from its inorganic and indestructible character is apt to accumulate in a yard in which it is used. The same reasons render unadvisable its introduction into any liquors which are to be returned to the leaches even in the tannage of dressing leather, though its presence in the colouring liquors is otherwise very useful in lessening the astringency of the tannins (" mellowing the liquors "), and making a fine grain. Its mode of action is by no means clearly explained, but is in some way connected with its tendency to produce " conjugated acids " (*L.I.L.B.*, pp. 37, 46).

The so-called " mellowness " of old liquors requires a word of comment. It is well known to practical tanners that old liquors are much less liable to produce drawn grain, and a harsh surface, when used to colour green goods, than liquors, even equally weak, which have been made from fresh materials. This is due to more than one cause. Most natural tanning materials contain tanning matters of varied degrees of astringency and power of attaching themselves to the leather-fibre. It is obvious that if a tanning liquor is used the most astringent and energetic tannins will be first removed from it, leaving those of a milder character. It is also known that the presence of neutral alkaline salts of weak acids has considerable influence in producing mellowness ; the addition, for instance, of sodium acetate has a marked effect.

This effect is probably due in the first place to the action of neutral salts in diminishing the energy of weak acids (see p. 99), and secondly to the fact that their bases combine to some extent with the tannins ; and that, as was perhaps first pointed out by the writer, such tannins are, as it were, partially paralysed in their action on hide, since tannin will not combine with hide in an alkaline condition (p. 118). Sodium sulphite acts powerfully in this way, and may perhaps prove of technical value in temporarily diminishing the astringency of liquors in quick tannage. Borax has a similar effect, but is too alkaline, and, unless used with extreme caution, spoils the colour of the liquors by causing oxidation. It is probable that similar causes explain the mellowness of palmetto extract, which contains large quantities of alkaline salts and non-tannins, and of some extracts which have been treated with sulphites, when used undiluted in drum-tannage. The addition of free acid will generally restore these tannins to an active condition.

J. A. Wilson[1] has recently shown that much of the mildness of mild tans is due to the non-tans and weak phenolic acids which they contain. Thus quebracho, which is a very rapid and astringent tan, with the lowest non-tannins of any in use, becomes as mild and slow as gambier, in which the non-tans are very high, if a quantity of gallic acid proportionate to the difference be added to the quebracho.

As the tannage proceeds and penetrates further into the hide the liquors are used stronger, as the outside, once tanned, is to a large extent protected from their action, and it is only by continuously increasing the strength of the liquors that more tannin can diffuse into the interior, since diffusion only takes place from a stronger into a weaker liquor. The liquor in the interior of the butts is always exhausted of tannin so long as any part of the hide-fibre remains untanned, but as the layer of tanned fibre between this and the outside gets thicker, a greater difference is required to maintain a reasonable rate of exchange, just as a greater head of liquor is required to maintain a flow of liquor through an increased number of percolation-leaches. If the strength of the liquor outside be allowed to fall off, this graduation of strength from the outside to the inside of the butt is disturbed, and takes some time to re-establish. As the liquors become stronger in tannin they may also become somewhat stronger in acid, since, as has been stated, the two act to some extent in opposition to each other. The acid-swollen fibre absorbs the tannin more slowly than if it were in more neutral

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[1] *Journ. A.L.C.A.*, 1920, p. 295.

condition, but it absorbs it apparently in larger quantity, and at any rate makes a firmer, more solid, and less flexible leather.

It has been mentioned that in the latter stages of the process solid tanning materials are generally strewed between the butts in the tanning liquor. It may be pointed out that many materials vary in their tanning effect, according to whether they are used in solid form or merely in liquors. It has been shown by Youl and Griffith [1] that such materials as valonia, oakwood and chestnut extracts, and myrobalans, which contain both gallotannic and ellagitannic acids, lose strength rapidly when kept in the form of liquor, and still more rapidly when heated,[2] the ellagitannic acid becoming decomposed with separation of insoluble ellagic acid. Now it is just this ellagic acid which, deposited *in* or *on* the leather, gives weight, solidity, and bloom, and the investigation points out not only an important source of loss in the tanning industry, but also explains why valonia, which in sole leather tannage is known to give hard and heavy leather, can be used in large quantities on dressing leathers in Yorkshire, with gambier, in the form of liquor, giving a soft and mellow leather almost destitute of bloom. In this case the valonia is extracted by boiling, and the liquors kept long on the material. If weight and solidity are required from the use of such materials, it is obvious that they must be brought into immediate contact with the leather to be tanned, so that as large a part of the bloom as possible is deposited in, and not outside the leather. With many other materials, such as hemlock, quebracho, and mimosa, which yield no bloom, but "difficultly soluble" tannins (reds or phlobaphenes), the same rule holds, since in contact with the hides the small proportion of these materials which is soluble in the liquors is replaced from the materials as rapidly as it is absorbed by the leather, while, when liquors or extracts only are used, the greater part of these solidifying and weight-giving constituents remain unutilised in the spent tanning materials. At the same time the long "layers" afford an opportunity for the acetic and lactic fermentations to go on which are the principal source of the natural acidity of liquors. It must be understood that what are called layers in England are not to be identified with the *Sätze*, but rather with the *Versenke*, of the German tanner, the former being layers given in much the same manner as was current in England 150 years ago; in which the

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[1] *Journ. Soc. Chem. Ind.*, 1901, p. 428.

[2] For the same reason bloom-yielding materials must be extracted for analysis at as low a temperature as possible, and some tannin is always destroyed at 100° C.

leather, with thick layers of tanning material between, is laid in the empty pit, which is afterwards filled up with liquor, often of a comparatively weak character. In such layers the acidification and the solidification of the leather both go on to a still greater degree ; the acid formed apparently gradually penetrating to the heart of the leather-fibres, and producing a solidity and cheesy texture which can hardly be obtained by layers of the English kind, which nevertheless have the advantage in rapidity and cheapness.

In drying sole leather, one of the great objects which must be aimed at is to remove the dark-coloured liquor, with which the goods are saturated, from the surface, and to prevent further portions of it from finding their way there from the interior. If a strip of filter-paper be allowed to rest with one end in a basin containing a little liquor and be placed in a draught of air, the exposed end of the paper will rapidly become dark brown or black, the liquor which evaporates there being constantly replaced by fresh portions sucked up by capillary attraction from the basin. A similar action is constantly seen when filtering liquors through paper if the latter be allowed to project above the edge of the funnel. Precisely the same effect occurs, perhaps increased by the oxidation of the tannins, on the edges and other parts of a butt which are most exposed to draughts of air. The use of oiling the grain is not only, to a certain extent, to protect it from oxidation, but also to check evaporation, and the consequent accumulation there of the dark-coloured solids contained in the liquor. A very similar result is attained by wetting the grain side, and allowing as much of the evaporation as possible to take place from the flesh.

As the finishing is almost purely mechanical, and scarcely comes within the scope of the present volume, a very brief sketch must suffice. The mode of finishing which was formerly, at least, in vogue in Lancashire and Cheshire may be taken as a type of the best work. (In the present day the various methods are so widely known that they have ceased to be local, and are varied according to the quality and tannage of the goods.) The butts, which in earlier times were largely bark-tanned, are taken wet from the pits, and scoured on a rounded beam or " horse " with stone and brush till the bloom is completely removed, and are then lightly oiled on the grain, half dried (" sammed "), laid in pile to temper, and " struck out " with the " pin," a two-handled tool of triangular section. The use of this tool has now been largely superseded by Wilson's striking machine, in which knives or sleekers (or stones and brushes), held in jointed arms, are made to work on the butt, which is extended over a slowly rotating cylinder. The object of the pinning is not so much to remove bloom or dirt, which has been previously effected by the scouring, as to smooth and flatten the grain. After further drying a second pinning is generally given, and the goods are then twice rolled, first with a light weight and somewhat moist grain, and then more heavily with the grain nearly dry. This was formerly accomplished by a sort of box or car, heavily loaded with weights, supported on a smooth brass roller of about 5 inches diameter and 9 inches long, and manipulated with a long wooden handle on a floor of hard wood or zinc plates. One type of the machines which have now almost entirely replaced this primitive contrivance is shown in fig. 77, but is principally used for offal and common classes of goods. For better work, traversing rollers, such as Wilson's ingenious double-bed roller shown in fig. 78, are to be preferred. After rolling, the goods are dried pretty rapidly by the aid of moderate heat, and, after polishing with a brush (hand, or machine, fig. 79), are ready for sale. It may be pointed out that although the tools are different, the process is almost the same as that used for "*vache lissée*" in France and Belgium, and closely resembles that of currying harness leather, except that the "stuffing" with fats and oil is omitted.

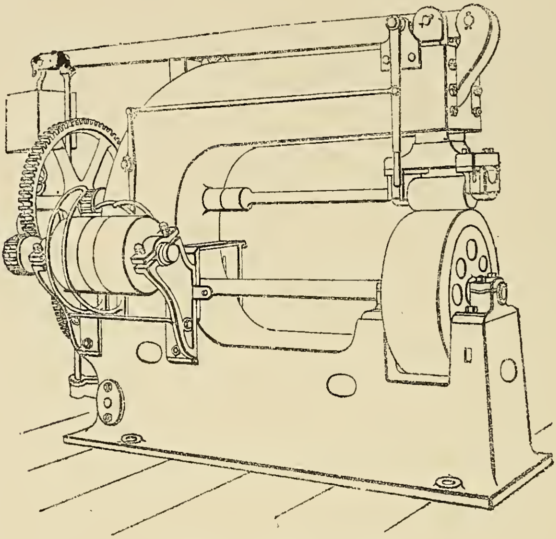

FIG. 77.—Offal Roller.

In contrast with the rather elaborate method just described we may place the American finish of red hemlock sides, which

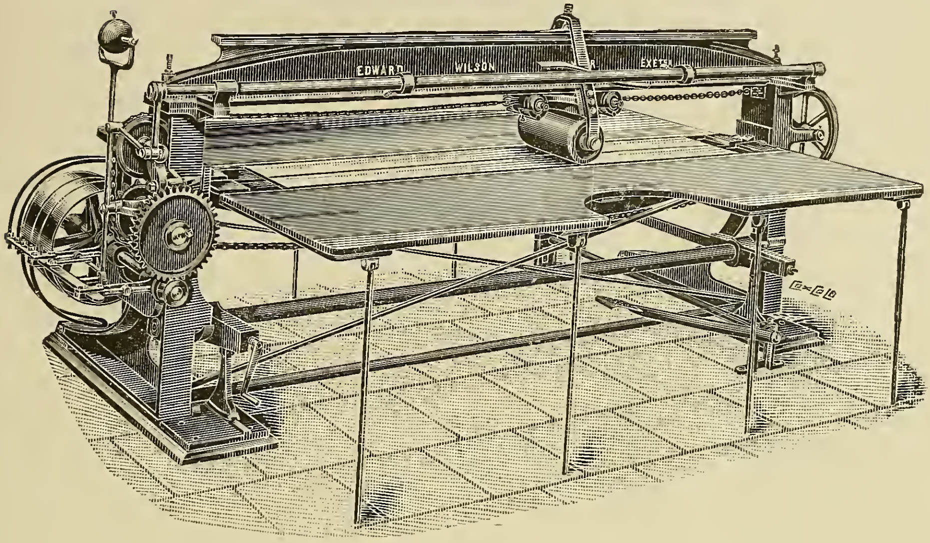

FIG. 78.—Wilson's Double-bed Butt Roller.

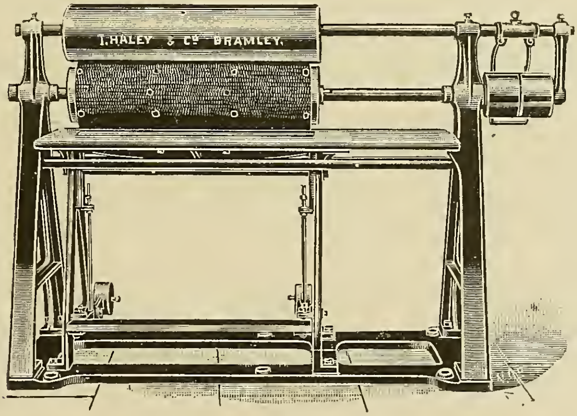

FIG. 79.—Brushing Machine.

are tanned throughout with a material which yields no bloom. On these, the scouring and "striking" is altogether omitted: the goods are completely dried out from the pits, which is found to fix the dark-coloured liquor, and result in better colour; they are then damped back, and tempered, and heavily rolled under a rapidly moving pendulum roller, which polishes at the same time that it smooths the leather. The saving of cost by so simple a process is not inconsiderable, and somewhat similar methods are gradually being adopted in this country, rolling taking the place of striking.

In the West of England much heavy leather has been manufactured from South American hides tanned with a large proportion of valonia, and which consequently are heavily bloomed. No attempt is made to remove this bloom, which would too much lessen the weight and firmness, but the goods, after a light oiling to preserve the colour, are hung up and partially dried, and are then laid in pile to temper. The grain side is now wet with soap and water, with which a little oil is often mixed, and the bloom is " struck in " with the pin or machine—a somewhat blunt pin being used, or a blunt tool in the striking machine—which is held at such an angle as to smooth and compress the grain without taking too much hold on it. After a little further drying the striking is generally repeated, the goods are washed over with water, and rolled " on." They are now coloured with a mixture of pigment colour, generally containing a large proportion of whitening, or sometimes of French chalk coloured with ochres, chrome-yellow, and orange, or whatever may suit the tint preferred by the tanner, or best imitate the colour of a clean-scoured tannage, and usually mixed with size and oil, or sometimes with oil and tan liquor. This mixture is well rubbed in, and smoothed over with a cloth, and then polished by brushing, when the goods are " rolled off," rapidly dried, and again brushed. If the work has been well done, it is not easy to distinguish from clean scouring, and is much cheaper.

A method intermediate between this and the first described, and which was formerly much used in London, was to proceed as above, but using more water and holding the pin in the first striking so as to scour out as much bloom as possible, and assisting this by the free use of water and the brush. Instead of using an opaque pigment-colour the goods were generally coloured either between striking and the first rolling, or between the two rollings, with a transparent colour, such as dissolved annatto, or a mixture of aniline dyes, so as to conceal the traces of bloom, and to render slight damages to the grain less conspicuous.

The process of sole leather tanning has been discussed in considerable detail on account of its simplicity and importance. It is now time to point out in what respects the tannage of the lighter leathers differs from it in principle. Taking the case of ordinary dressing leathers, such as kips and shaved hides, the first point to remember is that these goods come into the liquors not merely almost entirely deprived of lime by bating, but in a very flat and fallen condition from the action of the bacterial ferments of the bate. As a general rule in this country the colouring is done in paddles, but where a very smooth grain is required the use of suspenders is to be recommended, and in America is largely adopted. Indeed in the States the entire tannage of much of the cheaper leather is done in suspension, and the sides are only removed from the laths to which they have been nailed when they are required for splitting. It is obvious, from what has been said of sole leather, that as the hides are brought into liquors in a very fallen and extended condition, the grain will be likely to be wrinkled; and indeed this is sure to be the case unless, by suspension, the hide is more or less kept in tension till its fibres are fixed by tanning. The free motion in the paddle favours the formation of a "pebbled" grain, since the hide is bent now this way now that, and minute wrinkles and creases are formed in all directions. For many purposes, and especially if a grain is afterwards to be raised by "boarding" the curried leather, this graining in the paddle is not disadvantageous so long as it is not excessive. In some other cases it causes much trouble and labour to the currier before it is removed, and if the English tanner and currier are ever to compete with the American in smooth grain finishes, it will be necessary for them to obviate this source of wasted labour. The graining is the less considerable, and the easier to remove, the weaker and more mellow are the liquors employed in colouring and the more gradually their strength is increased.

The production of a soft leather depends on the fibre being tanned in a fallen and unswelled condition. It is for this reason, and to remove the elastin-network from the grain-layer, that bating is in many cases essential, though where somewhat firmer leathers are required, mere reduction of the swelling by removal of the lime is sufficient. For the same reason no acid-swelling is permissible either before tanning or in the liquors, and though liquors for soft leathers must be faintly acid, they are incapable of removing any large quantity of lime, and for the best results the deliming must be complete before tanning.

Now that in the light of knowledge very recently acquired we have much clearer ideas than formerly of the exact objects of bating and puering, it ought in many cases to be possible to dispense with these operations altogether in favour of a scientific system of deliming and reducing the alkaline swelling. At a certain definite degree of acidity, the "isoelectric point," which for gelatin is about $P_H = 4{\cdot}7$, and for hide is almost identical, as Porter has recently shown (see footnote, p. 578), the hide-fibre is in a neutral condition, acting neither as an acid nor an alkali, and at the same time is in the least swollen condition possible by merely chemical neutralisation. It would be impossible to maintain this condition by the mere addition of any tolerably strong acid, but, taking advantage of the properties of weak acids and of their neutral salts (p. 99), it can be done, and would be very approximately attained by mixtures of acetic acid and sodium acetate, the P_H of which is little varied from 4·7 by small additions of acid or alkali, but it is very possible that better and cheaper solutions may be devised. The concentration would be regulated and maintained by the addition of small quantities of acid or of sodium acetate to the neutral point of alizarin red, which closely corresponds to the isoelectric point (*cp.* p. 201), using the comparator if the liquor is coloured. Such regulating salts are usually called "buffers."

Another result of puering is the digestion of the elastin of the grain and of any remnants of the glands and hair-follicles which remain, and this would be done if necessary by pancreol or some other tryptic ferment, in mixture with ammonium chloride, and preferably before the neutralisation, as these act most favourably in a somewhat more alkaline solution, indicated approximately by the neutral point of cresol red. The ammonium chloride itself acts as a buffer.

As mere bating or puering is mainly designed to reduce swelling by the action of bacterial products (p. 218), and is not a very efficient means of removing lime, it is desirable where it is employed, to supplement it by some more active deliming process. In the lighter leathers drenching (p. 214) generally fulfils this purpose, and many of the more intelligent tanners now give bated hides a bath in boric acid before tanning, which not only removes the last traces of lime without acid-swelling, but checks the bacterial fermentation, and prevents its introduction into the liquors. In gambier tannages, a decidedly better colour is obtained by this treatment (p. 362).

In most cases the production of bloom is not desired in dressing leather tannage, and is prevented by relying chiefly on liquors, and avoiding the use of bloom-giving solid materials, which include most pyrogallol tannins. Dressing leather tannages can frequently be advantageously hastened by drumming, which by continuously bending the leather in all directions constantly widens and contracts the spaces between the different fibres, and, as it were, pumps the liquor through the skin, but of course tends to produce a "pebbled grain." The softness of dressing leathers is increased, and the hardening action of acids present in the liquors is prevented by the addition of salt, or of some sulphates (sodium, magnesium, ammonium) which exercise a sort of pickling action on the fibre and prevent its swelling, but at the same time tend to light weight and a somewhat empty tannage. It by no means follows that a hide or skin which is thoroughly coloured through is really fully tanned ; as, though the fibres may be actually tanned or coated on the surface, time is required for the tannins to penetrate them to the centre. This incompleteness of saturation is often found in drum-tannages. Such leathers are generally tough, and gain weight and softness in currying. In order to "carry grease" well, that is, to absorb a large quantity without appearing greasy, it is essential that the fibre bundles should be thoroughly split up or differentiated ; and the degree to which this is attained largely depends on the extent of liming. There is also considerable difference in different tannages as to the amount of grease which they will carry.

It is now not uncommon to combine a degree of alum or chrome tannage with vegetable tannage in the finer dressing leathers. For further information on this the reader must be referred to the next chapter.

The finest sorts of leather, such as goat, calf, sheep, and seal, for bookbinding, upholstery, and the like, are mostly tanned with sumach, paddles and drums being largely used to quicken the operation. Leather tanned with sumach has been proved by the researches of the committee of the Society of Arts on the decay of bookbinding leathers [1] to be the most durable leather for this purpose, some other tanning materials of the pyrogallol class coming near it in this respect, while all catechol tannages are found peculiarly liable to destruction by the action of sunlight, dry heat, gas fumes, and traces of sulphuric acid from other sources, although in many cases more durable than the pyrogallol tannages when merely exposed to mechanical wear and moisture, as is the case with shoe leather. East India sheep- and goat-skins, so-called "Persians,' are tanned with the catechol tannin of *Cassia auriculata* (turwar, tarwad, or avaram) bark, and are very easily affected by light, so much so that a photograph can be printed on them in sunlight from a negative (p. 329).

The finer leathers of which we have just spoken are almost

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[1] *Soc. of Arts Journ.*, 1901, p. 14.

invariably prepared for tanning by puering and drenching, as colour and softness are the principal characteristics aimed at. A somewhat interesting style of tannage is occasionally used for sheep-skins (roans) and calf-skins, in which the skin is sewn into a bag, flesh side out, with only a small aperture left for filling in one of the shanks. It is then turned grain side out and filled with strong sumach liquor and a little leaf sumach to prevent leakage, and floated in a tank of warm sumach liquor. After a short immersion the skins are piled on a stage, so that the liquor is pressed through them by their weight, and when partially empty they are refilled, and the process repeated. The tannage is complete in about twenty-four hours, and the leather is very soft.

Although the various chemical and physical theories of the tanning process are discussed at some length in Chapter XXXII., it may not be out of place here to point out certain chemical facts which are not in dispute, and of which the knowledge may help to make clear the reasons governing the methods of manufacture which have just been described. In the preparatory processes through which the skin has passed, whether for sole or dressing leather, the conditions have been prevailingly alkaline, and even if acid deliming is practised, the aim is rather to bring the skin to a neutral than an acid condition. For the actual tannage, however, it is essential that the reaction should be acid, though the actual degree of acidity as measured by the hydrion concentration will vary much with the class of leather produced, being somewhat considerable in the case of sole leather, and but little on the acid side for the finer and softer leathers. Whatever the nature of the combination of tannin and pelt it only takes place in acid solutions, and though it is easy to bring the difficultly soluble tannins, such as the "reds" of quebracho, into alkaline solution, they fail to tan in that condition, and recourse must be had to such salts as bisulphites, which, while they have an acid reaction, are so weakly acid that their bases (soda in the case mentioned) can form soluble salts with the weak acids of the difficultly soluble tans. As to the reasons for this peculiarity Chapter X. must be consulted, but it may be pointed out here that alkaline liquids not only do not tan, but actually "strip" the tan already deposited, and this is even true to some extent of bisulphites. Apart from this effect on the tannins, the acids, especially in sole leather tannage, have of course a direct effect on the skin itself, swelling and separating the fibre bundles of the corium into their constituent fibrils, and so presenting a larger surface to the action of the tan, and facilitating its penetration. In the earlier stages of the tanning process the untanned and freely exposed fibres combine eagerly with the tannin, and while weak liquors are sufficient to supply this, very large volume and rapid change of liquor is required to properly feed the skin. A large proportion of the total tan is absorbed in the first weeks of the sole leather tannage, and of course in still shorter time by the thinner leathers, and this emphasises the importance of rapid and continuous feeding in this stage. There is no reason to doubt that the tannin combines instantly with the raw gelatinous fibre when it comes in contact with it, but as the tannage progresses and the outside fibres are saturated, the liquor can only get at the fibres within by a slow process of diffusion, which is probably rendered still slower by the tanned surface acting as a more or less "semi-permeable layer." Now, diffusion can only take place from a stronger to a weaker solution, and hence the necessity of continuously increasing the strength of the liquor so that it should always be stronger than that contained in the tanned outer layer, and this continues to be true throughout the process. If the barkometer-strength of a liquor be taken at intervals, it will be found to diminish rapidly at first, then more slowly, and finally to remain almost constant, while the tannage at the same time comes to a standstill. One of the reasons, beside the greater strength of the liquors, why modern tannages are much shorter than they used to be is, that more care is taken that the liquors are changed before they have ceased to act, and there is no doubt that in the old two-years' tannage of sole leather much time was wasted in long layers, in the latter part of which little or no progress was made. Most rapid-tanning processes depend on the quickening of diffusion by mechanical means. Thus the drum-tannages, by constant flexure of the hide, alternately compress one side or the other, and thus produce a sort of pumping action, which forces the liquor through; in "bag-tannage" and some similar processes the liquor is forced through by direct mechanical pressure; while in the Nance High Vacuum process [1] the liquor, though only at a temperature of 70° to 80° Fahr., actually boils in the interior of the hide, and so produces rapid interchange.

In the earlier stages of tanning the liquors penetrate the

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[1] The attempt to force liquor into hide by direct pressure or moderate *vacua*, as is done in the creosoting of timber, has always resulted in failure, as the pores of hide are filled with practically incompressible water, while those of timber contain air. If the partially tanned hides were dried before impregnation, liquor could easily be forced through them in this way.

fibrils and combine with them (whether chemically or by "adsorption"), and render them incapable of swelling in water or of putrescence, and actually converted on the surface into leather,[1] but such leather is porous and light-weighing, and quite unsuitable for practical use, especially as sole or belting leather.

As the tannage progresses the fibres may be assumed to be completely converted into leather, but they are still capable of fixing tannins, and especially the less soluble tannins, and such bodies as ellagic acid, by adsorption or crystallisation, and the leather gains in weight and in firmness, but this part of the process must be very limited in dressing leathers. The case is very parallel to that in the chrome process, where, after the first stages, only the more basic and less soluble salts are fixed. After the completion of the tannage in the yard it is very customary to "vat" the leather in the case of sole leather in strong and warm solutions of highly sulphited extracts, but this must rather be considered a bleaching than a tanning operation, as its effect is to remove a part of the phlobaphenes and difficultly soluble tannins which have been deposited, and to render the leather softer and more porous and permeable to water. In dressing leather yards where mixed tannages are used it is customary, with a similar object, to drum the goods in a warm sumach or myrobalans liquor, but this with the lighter leathers is more defensible.

Even when the goods are removed to the shed the tannage can hardly be said to be quite complete, as no doubt further fixation of the soluble tannins goes on during the drying, and some of the non-tanning matters, such as gallic acid, undergo oxidation and dehydration, and exert a tanning effect if the fibre is not already fully saturated (*cp.* p. 574).

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[1] In this stage the microscope shows no signs of a mere *coating* of the fibres such as Knapp supposed.

CHAPTER XXII

COMBINATION OF VEGETABLE AND MINERAL TANNAGE

In very early times leathers were produced which were partly tanned with alum and partly with vegetable materials. One of the earliest of these was probably the Swedish or Danish glove-leather. The principle has long been applied to the production of certain very tough and flexible leathers known as "green leather," and used for "picker-bands" for looms, laces for belting, "combing-leathers," and some other purposes where softness and toughness are of principal importance. It was applied in America by James Kent to the manufacture of an imitation of glazed kid, which he named Dongola leather; and since that time the method, in various modifications, has taken a considerable place in the manufacture of the finer leathers for shoe purposes, especially in the United States.

Alum-tanned leathers, as has been already stated, are remarkable for softness and toughness, and the mineral (crystalloid) tannages have the power of penetrating and isolating the individual fibrils of the skin in a much greater degree than the vegetable tannins, and hence are less dependent than the latter on a previous isolation produced by liming or swelling. On the other hand, they give much less plumpness and solidity and more liability to stretch, and, as a general rule (to which chrome-tannages are an exception), are less resistant to the action of water, and incapable of producing a soft leather without mechanical softening (staking) after the tannage is completed. Purely mineral tannages have always a woolly fibrous structure, and never the firm and compact flesh which is required in leathers which are to be "waxed" or finished on the flesh side to a smooth surface, and as they communicate more or less of these peculiarities to combination-tannages, the latter are mostly used, either for grain-finish, or for uses where a soft and velvety flesh side is required, as in the case of "ooze" or "velvet" calf. On the other hand, the partial use of vegetable tannage communicates to them a degree of plumpness, fulness, and resistance to water which is not possible to alum-tannages pure and simple, and a softness which is not easily obtained in vegetable tannage without the use of large quantities of fats or oils. A preliminary mineral tannage also greatly increases the rapidity of the penetration of the vegetable tans, by isolating the fibres, and rendering them less gelatinous. Once a leather is *thoroughly* tanned by vegetable materials, it is little affected by subsequent treatment with alumina, or even with chrome; and, on the other hand, though chrome and alumina leathers are still capable of absorbing considerable quantities of vegetable tannins, they always retain, in a degree, the qualities which the mineral tannage has communicated to them. The resulting leathers are thus not only modified by the different proportion of vegetable and mineral tannages which have been given, and by the properties of the particular vegetable tannage used, but by the order in which the several treatments have been given, and always retain, to a considerable extent, the characteristics of that which has been first applied. We have thus in our hands a powerful means of modifying the character of our leather to suit the special requirements which it is to fulfil.

So long as tanners were restricted, on the one hand, to the ordinary methods of stuffing tanned leathers with oils and fats, and on the other to the use of egg-yolk, which had long been common in alum-tannages, combination-tannage remained of but secondary importance, and it was the application of the method of "fat-liquoring" by James Kent to his Dongola[1] leather which gave them the place they now possess, by providing a cheap substitute for egg-yolk, and enabling the tanner to obtain softness and resistance to water without producing the greasy feel which is common to curried leathers. The process of fat-liquoring has already been mentioned in connection with chrome leathers, to which it was subsequently applied, and we shall return to it after having given some further details of the methods of tannage.

In the first place, we must consider briefly the mutual action of the mineral and vegetable tannages on each other. It has been pointed out by Eitner, and also mentioned in connection with the decoloration of extracts (p. 405), that the addition of ½ per cent. of alum or aluminium sulphate to tanning liquors lightened their colour, not only by giving a degree of acidity to the solution, but by precipitating a portion of the darker and less soluble constituents, and made the solutions yellower by developing the colour of the flavone mordant dyestuffs which are contained in most tanning materials. It is therefore desirable, if these salts are used, to allow the solution to subside, or to filter off the dark-

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[1] "Dongola" leather was invented in the time of the Egyptian War, when Dongola was much in the public mind, hence its fancy-name.

coloured precipitate. Chrome and iron salts no doubt produce a similar effect, though from the dark colour of their compounds with tannins the lightening of colour does not take place. Potassium dichromate, especially if acidified, generally precipitates, oxidises, and darkens tannins, so that it is not practicable in combination-tannage (pp. 495, 506) to follow a vegetable by a two-bath chrome tannage, though the reverse order may be pursued.

Combination-tannages, such as the Swedish and Danish glove-leathers already referred to, are generally first tawed with alum and salt, with or without flour and egg-yolk, and are then coloured and more or less tanned with vegetable materials. That employed on the original Danish leather was willow bark (of *Salix arenaria*). In France, where this willow is not found, the bark of the commoner *Salix caprœa* was substituted, and as it is much weaker in tannin, additions of oak-bark or sumach to supply the deficiency, and of madder to give a redder colour, were made to it. The dyeing of these leathers is frequently combined with the tannage, dyewoods or dyewood liquors being mixed with the tanning liquors. In the manufacture of glazed French kid, indeed, the process is so arranged, by brushing on dye-liquors mixed with tannins, as merely to tan the grain-surface, which is necessary to enable an alumised leather to be glazed by friction, leaving the substance of the leather of purely alum tannage.

On the other hand, in the "green leathers" (so called from their greenish-yellow colour, and largely made in the West Riding of Yorkshire) the hides usually receive a light gambier tannage, extending over a week or so in weak gambier liquors in handlers, and are then "cured" by handling in hot and strong solution of salt and alum, in which they are finally left all night, and then dried rapidly without washing out the alum, much of which consequently crystallises on the surface. This is slicked off, and the leather damped back, and heavily stuffed with sod-oil. If, however, the combination-tannage is properly carried out, it will stand liberal washing without losing the necessary alum, and of course a tougher and more satisfactory, though somewhat lighter-weighing, leather results. It is in many cases a better plan to combine the two tannages in one bath, mixing the alum and salt with the gambier, and handling or paddling the goods in the mixture. This is the plan usually adopted for Dongola leather in the United States. For skins which are to be glazed it is important that the *surface* should be tanned with the vegetable material, and the goods are therefore worked into gambier liquors, to which the salt and alum are only added after the tannage has made some little progress; while for dull Dongola, intended rather to imitate calf-kid, it is best for the alum and salt tannage to begin first. For goat-skins for glazed Dongola kid about 4 lb. of block gambier, $\frac{1}{2}$ lb. of alum, and $\frac{1}{4}$ lb. of salt are used per dozen, and the tannage occupies in all about twenty-four hours.

After the skins are tanned they are thoroughly washed out with tepid water to remove loose alum and gambier, and are then ready for fat-liquoring. As in the case of chrome leather, it is of great importance that this washing should be done thoroughly, as any remaining alum which diffuses into the fat-liquor will cause it to curdle. A treatment with a weak neutralising solution, say of hyposulphite, in the first washing would do no harm. If the washing is thorough, the more neutral the fat-liquor the better, but a more alkaline solution is less liable to curdle, and the original fat-liquor used by Mr Kent was the very alkaline liquor which had been used for washing chamois leather, and therefore contained a good deal of dégras. Now, soap and oil solutions are usually made for the purpose, and those described in the chapter on chrome tannage are quite suitable, though fat-liquoring is somewhat easier than in the case of chrome, and the better the oil is emulsified, the more satisfactory is the result. A sheet-metal cylinder with a piston covered with fine wire-gauze does good service as an emulsifier, and another method is to incorporate the oil thoroughly with a hot pasty solution of the soap, which can be diluted as required. If special soaps are made by the cold process (p. 427), they can be superfatted in making as required. Oils containing a little free oleic acid emulsify most easily, and sulphonated oils are also suitable. For glazed finishes it is a very common mistake to employ too strong a fat-liquor—even $\frac{1}{2}$ per cent. of soap and $\frac{1}{4}$ per cent. of oil will produce a very noticeable softening effect—but of course for dull finishes much more may be used. Leathers absorb the fat-liquor most readily in a sammed condition, but even if quite wet they soon take up the whole of the oil and soap, leaving only a little turbid liquor in the drum.

Not only combination-tannages but purely vegetable ones can be fat-liquored, and the process is now largely used for coloured calf and other leathers which are required to be soft and nourished without greasiness. Sesame (Gingelly) oil seems very suitable for this purpose. East India sheep and goat, though they do not generally appear greasy, are often so heavily oiled with this oil (up to 30 per cent. of their weight) that it is usually desirable rather to diminish than increase it, which may be done by washing with soap-solutions, preferably before aluming. Goods may be blacked while still wet with fat-liquor, but, except in the case of chrome combinations, should generally be dried out before dyeing, as this fixes the oil and soap on the fibre.

Many leathers are now made by being coloured and partially tanned with ordinary vegetable materials, and finished with a Dongola tannage with alum, salt, and gambier, and fat-liquoring. In the United States the tannage is often begun by suspension in hemlock bark liquors.

Imitations of Dongola leather can be made by treating East India sheep or goat, or other lightly tanned stock, with an alkaline solution, such as dilute borax, ammonia, or soda, similar to those used in neutralising chrome leather, but somewhat stronger, to strip a portion of the tan, and then retanning with alum and salt, fat-liquoring and finishing in the Dongola manner. In place of mere alum and salt a " neutralised " basic alum solution is used with advantage (p. 242).

" *Semi-chrome.*" An exactly similar process may be used, employing instead of alum a basic chrome liquor such as is used in the one-bath chrome process, and the substitution may be so complete that the finished goods are difficult to distinguish from full chrome, and may even stand a moderate boiling test ; and during the war this process was used by many tanners who thought it easier than " straight " chrome.

Chrome combination may also be made by retanning the chromed leather produced either by the one- or the two-bath process with vegetable materials, of which gambier or sumach seem the most suitable ; but considerable care is needed, as retannage, even with very weak liquors, deprives chrome leather of its stretch, and if carried to excess readily makes it hard and tender. It may, however, be useful for some mechanical leathers, where the stretch is a disadvantage, and for treating chrome splits so as to make it possible to " wax " them. Chrome leathers cannot be " stripped " by alkaline solutions, but may be by a solution of Rochelle salt (p. 572), or by oxalic acid (Lamb's patent, p. 571).

Various other sorts of combination are possible beside those of mineral and vegetable tannage, as, for instance, of formaldehyde with both mineral and vegetable tannages, of which many forms have been tried, between this and peat or humus tannage (Payne), the halogen tannages mentioned on p. 575, quinone tannage, and many others, but none of them have reached practical importance. Chrome and iron combination tannages are noted on p. 289.

CHAPTER XXIII

GRINDING OF TANNING MATERIALS

Before the tannin they contain can be extracted, most materials require to be ground, almost the only exceptions to this rule being divi-divi and algarobilla, in which the tannin is very loosely contained. Extracts, whether solid or liquid, merely require to be dissolved in water or liquor, in which they are, for all practical purposes, perfectly soluble. With the less soluble extracts it is generally preferable to dissolve at a temperature of 50° to 60° C. with vigorous stirring. For solid extracts some method of mechanical agitation is desirable.

The actual method of grinding, and consequently the machinery employed for the purpose, vary not only with the material to be ground, but with the method of leaching adopted, as it is essential that the mass of ground material should be completely permeated by the liquor employed in leaching; and if it be ground too finely, or subjected to too much pressure on account of the height to which it is piled in the leaches, it is apt to form a compact and clay-like mass, the interior of which remains unextracted. This is specially important in the "press" or circulating systems now generally adopted.

In the laboratory, where thorough extraction must be completed in a few hours, the material can hardly be too fine; but on the larger scale a much coarser product must be used, and leaching requires days, or sometimes even weeks, and is then seldom successful in removing all the tannin. It is probable, however, that in the future these mechanical difficulties of extraction will be overcome; and the material will then be as finely divided, and as completely extracted on the large scale, as it is in the laboratory at the present time.

One of the earliest methods of grinding oak-bark, and which is still used for sumach (p. 308), consists in crushing it under large circular edge-stones, frequently turned by a horse. This process was very slow and inefficient for barks, and both it and horizontal millstones similar to those used for wheat were long ago superseded by iron or steel mills on the same principle as the ordinary coffee-mill.

These mills (fig. 80) consist of a "bell" or inner cone, covered with blades or teeth arranged at a slight angle to the vertical section of the cone, and which are made finer and increased in number towards its lower and wider part. This cone rotates within an outer hollow cone or casing, also provided with blades or teeth which are sloped slightly in the opposite direction to those of the inner cone, so as to meet them at an angle, like the cutting-blades of a pair of scissors, and the angles of the cone are so chosen that the blades approach each other more closely towards their base. The outer cone is fixed, and is provided with a hopper like a coffee-mill, while the inner cone is so rotated on its axis that bark placed in the hopper is screwed down between the two, and cut finer and finer till it reaches the lower edge, when it drops out. The blades or teeth are usually cast in one piece with the metal cones, and sharpened when required by chipping with cold chisels. This operation should not be conducted in the mill-house, or small chippings of iron may get mixed with the bark and cause stains on the leather. This form of mill, which is run in England at about thirty revolutions per minute, and nearly three times as fast in America, works very well with dry material, but clogs badly if it be appreciably damp. On this account it is always well to run the mill with a fairly slack belt which will slip before exerting sufficient pressure to break the machine, as in such operations as grinding, safety-clutches are of but little use.

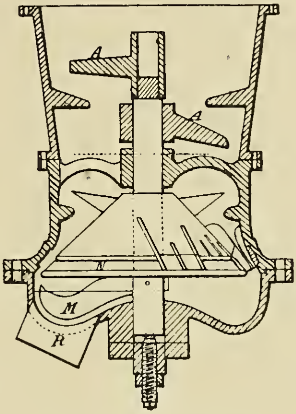

Fig. 80.—Cone Mill.

A type of mill varying somewhat from the above consists of a pair of discs or very obtuse cones, the inner one of which runs on a horizontal axis. The teeth are generally arranged in concentric rings and interlock with each other, so that the operation of these mills is a direct "shearing" and not a clipping one. The material to be ground is fed at or near the centre of the fixed disc, and escapes at the edges. The construction of this class of mill will be easily understood from fig. 81. With damp materials the discs very readily become clogged between the teeth, and small pieces of iron or steel which get caught between the teeth will often result in the breaking of the latter and the formation of iron dust, which is a serious objection to the employment of this type of mill (to which the Schmeija " Excelsior," the Glaeser " Favorita," and the " Devil Disintegrator " of the Hardy Patent Pick Co. belong) for grinding barks.

Myrobalans and mimosa barks have proved especially troublesome to grind, the former from the hardness of the stones of the fruit and a tendency to clog the mill, and the latter from their combined hardness and toughness. " Disintegrators " of various patterns are now made which are capable of grinding both these materials satisfactorily, and, but for their liability to cause fire, and the larger proportion of fine dust which they make, are usually to be preferred to toothed mills. For these reasons the mill-house should as far as possible be isolated from other parts of the tannery. In spite of their disadvantages, however, they have come very largely into use on account of their efficiency in grinding obstinate materials. Disintegrators work on the principle of knocking or beating the material to powder by means of very rapidly revolving beaters, which, in the smaller machines, are driven at 2500 to 3000 revolutions per minute.

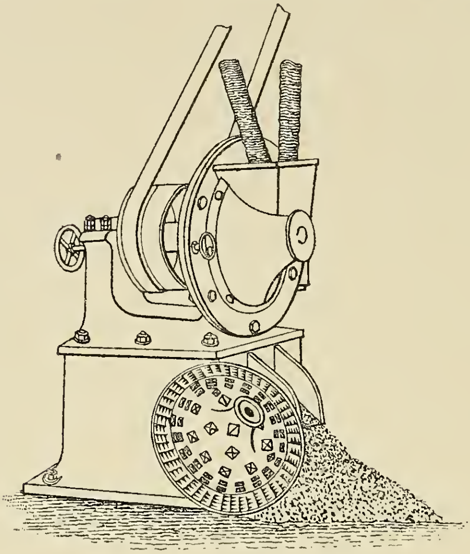

FIG. 81.—" Excelsior " Mill.

The first disintegrator was made by Carr, and consisted of two concentric cylinders or baskets of steel bars rotating in opposite directions at a very high speed. The material was fed between these, and was dashed to pieces by being thrown against the bars and the outer casing.

A simpler form was soon introduced by Carter, in which only one axis was employed, carrying radial beaters which dashed the material against the serrated outer casing, a portion of the circumference of which was fitted with gratings, through which the ground material was thrown as soon as it was sufficiently reduced in size, the fineness of the grinding being regulated by changing the grates as required. This type of disintegrator is, with slight variations, made by all the leading makers of tanners' machinery; and one form is shown in fig. 82, and a similar but smaller machine, opened to show construction, in fig. 83.

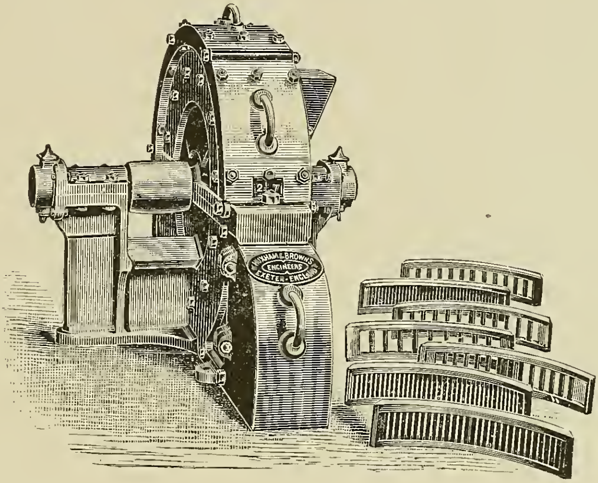

FIG. 82.—Disintegrator.

In the more modern machines the sides as well as the circumference of the casing are frequently corrugated in order to increase the action on the material.

Mills running at such high rates of speed as 3000 revolutions per minute will grind most hard substances, such as stone or brick, without injury, but pieces of iron among the tanning material are apt to cause damage, and various magnetic devices have been employed for separating this metal, but with only partial success. In the best mills, therefore, the beaters and inner casings are constructed so that they can be easily replaced, and the damage is then rarely serious.

In order to avoid vibration the discs and beaters of all these high-speed mills must be balanced with great accuracy. This is best accomplished by removing the spindle from the mill and allowing it to roll on two levelled straight-edges, and then filing or chipping the beaters on the heavy side until it will remain indifferently in any position.

A form of disintegrator has been brought out in America by the Williams' Patent Crusher and Pulveriser Company, in which

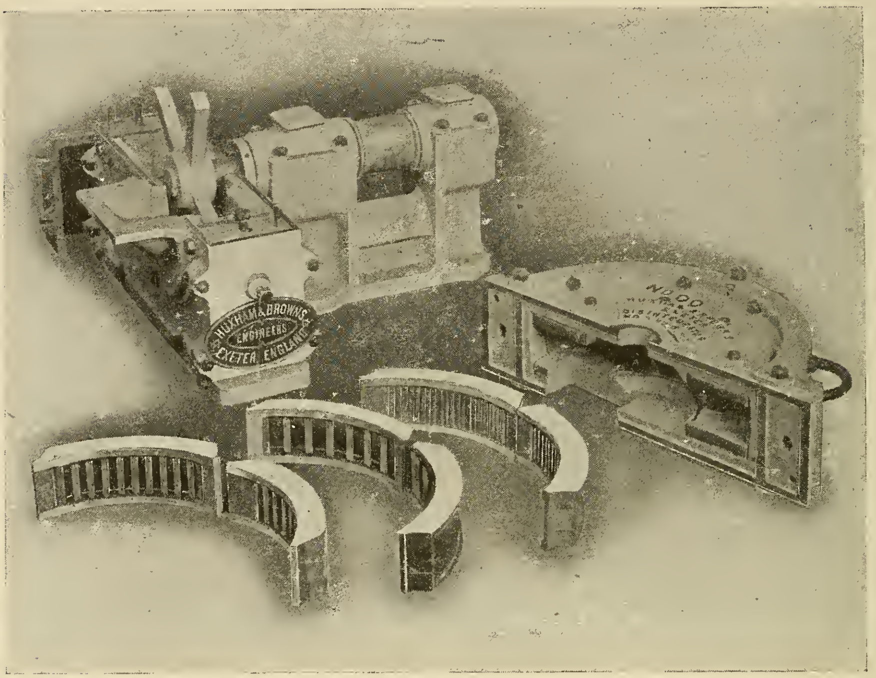

FIG. 83.—Disintegrator opened, showing construction.

a series of discs are keyed to the main shaft, to the circumference of which a number of sets of "hammers" are suspended by means of hinge-bolts. Each of these steel bars, or hammers, has a free arc movement of 120°, and when the machine is in motion take a position divergent from the centre on account of the centrifugal force. After striking a blow against any material fed on to a plate serving as an "anvil" the hammers recoil, and, after passing any material which is not shattered by the blow, again resume their normal position, leaving the next set of hammers to beat against the unground material. The hinged suspension of the hammers imparts a degree of flexibility to the mill which is not found in any other machine of this character, and lessens the risk of serious damage to the machine by the introduction of pieces of metal along with the bark. The makers claim that this machine can be repaired more rapidly and with less expense than any other disintegrator of equal power on the market. Considerable improvements have recently been made in the details of its construction. Fig. 84 shows a section of this mill. Of course only the end hammers of each set can be seen in the figure, and several improvements in detail have now been made.

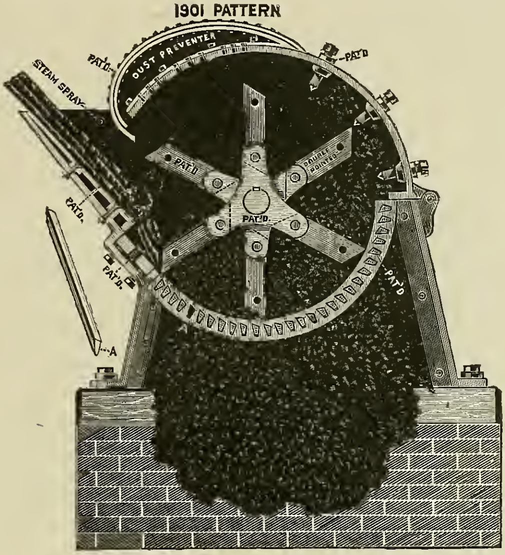

Fig. 84.—Section of Williams' Crusher.

It is necessary that the feeding aperture of disintegrators should be well protected to prevent the escape of fragments. The writer remembers the case of a girl who lost an eye through an escaping fragment of glue which was being ground.

When myrobalans or valonia is to be used for leaching, it is generally better to crush it between toothed or fluted rollers rather than to grind it finely, as the cellular structure is just as completely broken up, and the flakes formed by crushing allow of much freer percolation than when the material is powdered by the disintegrator, while the consumption of power is also less. The general construction of the machine will be easily understood from fig. 85, and it is only necessary to point out that the small upper roller acts mainly as a " feed " to the larger crushing rolls.

In the best mills the rollers are made up of a series of toothed steel discs on a square axis, and are on this account easily replaced or sharpened when they have become broken or worn.

Several mills have been introduced in America in which the bark is sawn or rasped by toothed discs like circular saws, but these are only capable of dealing with barks of a brittle nature, and are immediately choked by tough materials like the bark of the mimosa or oak. A better form of mill, but one which is, to some extent, subject to the same disadvantage, is the "shaving-mill," in which blades are fixed like plane-irons upon a disc, cones, or cylinder, and are rotated at a high speed against the material, which is fed against them by toothed rollers at such an angle that the shavings are cut diagonally to the grain. These shaving-mills are largely in use in America for hemlock bark, with which they are particularly successful. The principle of the machine is exactly the same as that of the machines used in cutting oak-wood, quebracho, and the different dyewoods. One type of shaving-mill is illustrated in fig. 86. Such machines are only suited for cutting rather thick bark in "long rind," and are quite unsuitable for chopped bark.

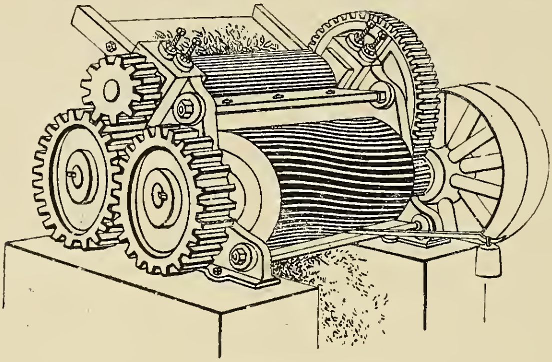

FIG. 85.—Myrobalans Crusher.

It frequently happens that the material is delivered from the mill in a very unequal state of division, and it is sometimes necessary to screen it and thus separate the coarser portion either for use in the leaches or for re-grinding, while the finer portion is more suitable for "dusting." With disintegrators, which deliver the bark with considerable impetus, the screening can be accomplished by placing a screen diagonally below the mill, through which the finer parts are projected. It is, however, essential that this screen should be quite smooth on its upper surface and very strong, as ordinary wire gauze is immediately cut through by the impact of the material. What are called "locked wire screens," in which the wires are supported by being actually twisted round the transverse bars, are very suitable. Where the circumstances will not permit of screening in this way, cylindrical rotating screens, or nearly horizontal screens vibrated by an eccentric, may be used. The latter are cheaper to erect, and have the advantage that they take up less room, and by having lengths of wirework or perforated steel of different coarseness the material may be separated into more than one degree of fineness.

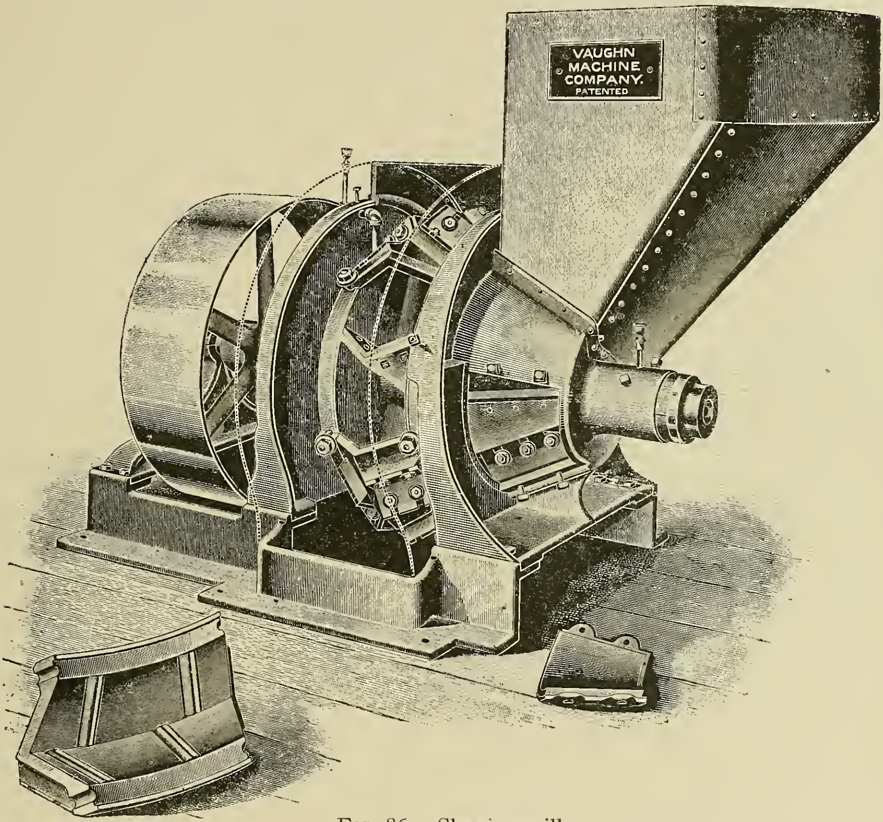

Fig. 86.—Shaving-mill.

Oak-bark as it is taken off the trees is usually in lengths of perhaps 3 feet, and it is necessary to cut or break it into smaller fragments before it can be ground in most of the machines just described. This is frequently done by hand by chopping the bark into pieces about 4 inches long, and the operation is known as "hatching." Machines on the principle of the chaff-cutter, consisting of a fly-wheel with curved blades radially attached to it, are sometimes used. Instead of "hatching" it, the bark is frequently broken by passing through toothed rollers fitting into each other, and often attached to the mill; the construction of this machine will be readily understood from fig. 87.

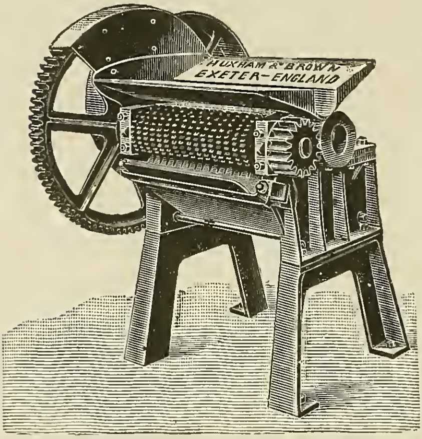

Fig. 87.—Bark Breaker.

In Belgium, and some other bark-producing districts, the adhering moss and dead outside bark are usually removed before hatching, but apparently these impurities are frequently re-mixed with the bark after the hatching is completed! As such barks often also contain much clay and dirt, it is generally expedient to pass the hatched bark over a coarse screen before letting it enter the mill, so as to remove the greater part of such rubbish, since, if left in the bark, it produces black and unsatisfactory liquors.

In drawing up policies for fire insurance it is usual to charge a higher rate where disintegrators are used to grind the tanning material, as, owing to the amount of dust and the production of sparks by the striking of the steel parts of the machine on any chance piece of flint or metal which may get into it, there is a greater liability to fire than with toothed mills, although with proper precautions the risk is really small (*cp.* p. 546).

All disintegrators act like ventilating fans, and suck in air with the material, blowing it out again with great force at the periphery. This air is heavily laden with dust from the tanning material, which is extremely irritating to the lungs. The difficulty is to some extent remedied by an air-channel or flue (generally cast in the casing of the machine) connecting the discharge with the feed-opening so as to convey the air back to the disintegrator. The air is thus circulated through the arrangement, but some is always drawn in from the external atmosphere and driven out with the ground material, and it is advisable that the chamber into which it is discharged should be provided with some means of filtering the air before it escapes. One convenient method is to have a large suspended flannel bag which is blown out by the air like a balloon and out of which the dust can be shaken when the machinery has stopped. Another efficient method is to have one of the walls or the ceiling of the chamber made of canvas or of sacking ; but in any case the air should be allowed an escape where a little dust will not cause annoyance.

Chain-conveyors.—While in England the ground material is usually carried from the mill to the leaches in barrows or baskets, in America the use of conveyors is practically universal, and there is no doubt that they effect a great saving of labour at a comparatively small cost.

The most practical conveyor for tanning materials consists of a trough through which an endless chain passes carrying scrapers. The chain generally used for this purpose is one consisting of square links fitting into each other and capable of running over toothed wheels. These chains are made by several firms in America, and in England by the Ewart Chain Conveyor Co. of Derby, who supply not only plain links but also those having projections to which buckets, scrapers, and a variety of attachments may be fixed.

In many cases the trough is V-shaped, with the chain running in the angle ; in others flat-bottomed, as in the illustration, or rectangular. The scrapers may consist either of metal or of wood ; and where materials have to be carried up a steep incline, buckets instead of scrapers should be employed. The arrangement of such a conveyor is illustrated by fig. 88.

A useful form of conveyor for dry materials consists in a woven cotton belt running in a smooth trough and with laths riveted across it at intervals. These laths should project slightly beyond the edges of the belt so as to prevent wear. Care must be taken with belts of this sort that the material does not get between the belt and the pulley.

Chain-carriers are often used for conveying the spent tan to the furnaces from the leaches, and occasionally for carrying skins.

Beside the malleable cast links which have been spoken of, and which are so arranged that they can be unhooked from each other when the chain is slack, various forms of malleable links are also available.

Several other kinds of conveyor are in use in corn-mills, spiral or worm conveyors which work on the screw principle being very largely used for carrying corn. They are not very suitable for tanning materials on account of the coarseness of the latter, by which the friction is greatly increased; they are, however,

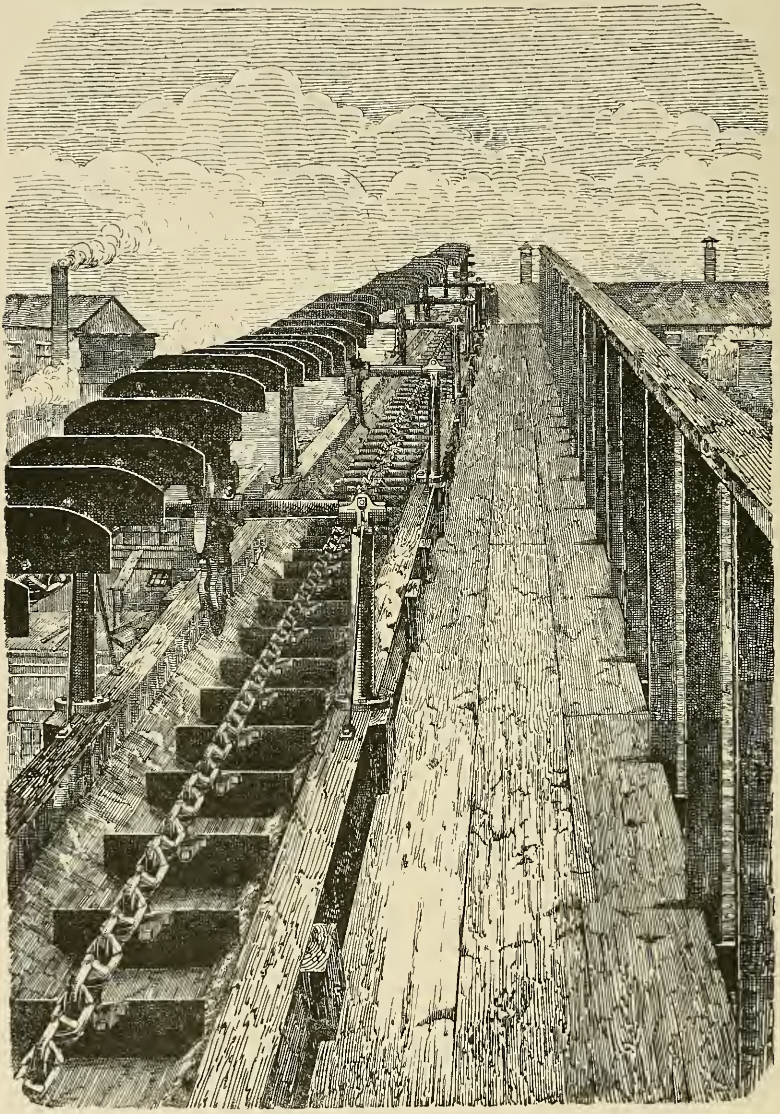

Fig. 88.—Chain-conveyor.

occasionally used. Those built up of separate blades are specially to be avoided. It must be remembered that while the smooth small grains of corn behave almost like a liquid, tanning materials, and especially rough ones like bark and valonia, have a great tendency to hang together, and even in hoppers with steeply inclined sides will not run down smoothly without shaking or stirring, but have a great tendency to hang back and form arches which do not fall in. Myrobalans is the only material which is pretty free from this difficulty.

An ingenious form of conveyor has been introduced from Germany, which consists of a light trough supported on steel springs, and vibrated longitudinally by means of an eccentric in such a way as to shake the material from one end of the carrier to the other, the velocity of motion of the trough being less in the outward than the return stroke, so that the material is carried with it as it moves forward, and slides over it in its return. It is obvious that the principle may also be applied to screening or sifting.

CHAPTER XXIV

THE EXTRACTION OF TANNING MATERIALS, AND THE MAKING OF EXTRACTS

Leaching.—The material having been reduced to a suitable state of fineness is ready for extraction. This requires a considerable amount of time, as the tannin is contained in cells of which the walls are of a wood-like substance (cellulose and lignine), through which the water diffuses but slowly. Hence, unless the material be very finely ground, a long soaking will be necessary before it becomes "spent." It should be the aim of the tanner to have his barks, etc., ground so finely that they may be extracted as rapidly as possible, and yet not be so fine that they settle to a compact mass in the leaches and so prevent circulation. Using the present methods of extraction on the large scale it is necessary to have the material only somewhat coarsely ground or crushed, so as to render its percolation practicable; but it is quite possible that in the future some better mechanical means will be found of treating the dust and other finely ground matter so as to bring about a very rapid extraction.

Several patents have been taken for continuous extractors, in which the material is fed in at one end of a long rectangular tank or trough and gradually moved forward to the other by spiral stirrers or some similar device, the extracting liquid being continuously run in at the end from which the exhausted material is removed, and means being supplied for suitable heating. It is possible that some such method may prove practicable for the treatment of finely ground material, but at present such machines seem either to require too much water and make too weak liquors, or not sufficiently to extract the material. Possibly they might prove useful in extract manufacture for a preliminary or a final treatment in conjunction with press leaches. An apparatus of this sort, under the name of "Automat," is made by Messrs Blair, Campbell & M'Lean of Glasgow. If used for the fresh material in extract manufacture, the liquors would probably require filtration.

Up to perhaps 180 years ago no attempt was made to leach the tanning material, which was simply strewed in layers between the hides and moistened with water. Leaching originated in England, and was first applied merely to complete the exhaustion of the material which had been already used for layers ; but the use of even weak liquors instead of water in the layers was found so advantageous, that new material was soon applied to make stronger infusions. The earliest form of leach was simply a pit with a perforated wooden " eye " or shaft down one corner, in which a pump could be placed to remove the liquor without being choked with solid matter. This was considerably improved by the addition of a perforated " false bottom " to the pit, with which the eye communicated. The perforations of the latter were found unnecessary, and it now serves simply for pumping through, or for the manipulation of a plug in a hole communicating with an underground " trunk " leading into a pump-well. The false bottom is best made of laths about 1 inch thick and 2 inches wide, cut slanting so as to be wider on the upper than the lower surface, which makes the spaces between them less liable to choke. The laths are nailed on cross-battens with copper nails, which should be long enough to clinch, $\frac{1}{4}$-inch to $\frac{1}{2}$-inch spaces being allowed between the laths according to the fineness of the ground material. The lattice bottom should be in at least two sections, so as to allow of its easy removal for cleaning, and should rest on detached blocks, which are best nailed to the underside of the battens. A space of 2 inches to 3 inches below the false bottom will prove sufficient if it is cleared every time the pit is emptied, but not otherwise. Clearness from obstruction both below the bottom and between the laths themselves is very important in securing free running in the " press leach " system about to be described. A section of the latticed bottom is shown in fig. 89. The laths are easily cut by employing a circular saw with a tilted table and turning the board at each cut. No advantage is gained by planing them.

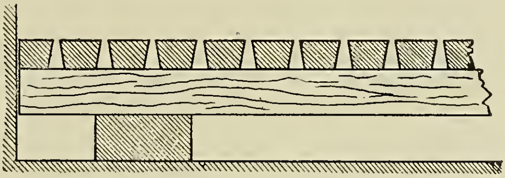

FIG. 89.—Section of Leach Bottom.

As a strong liquor cannot be made by the use of a single leaching pit, a series of pits are now always employed, and it is the leaching, systematic or otherwise, which determines how much of the total tannin will be thrown away and lost in the "spent tan." In the case of properly extracted materials the "spent tan" will not contain more than 1 per cent. of tanning matter, but the degree of extraction which is profitable is dependent on the tanning material employed and the class of leather to be produced. Weak liquors may of course be strengthened by evaporation.

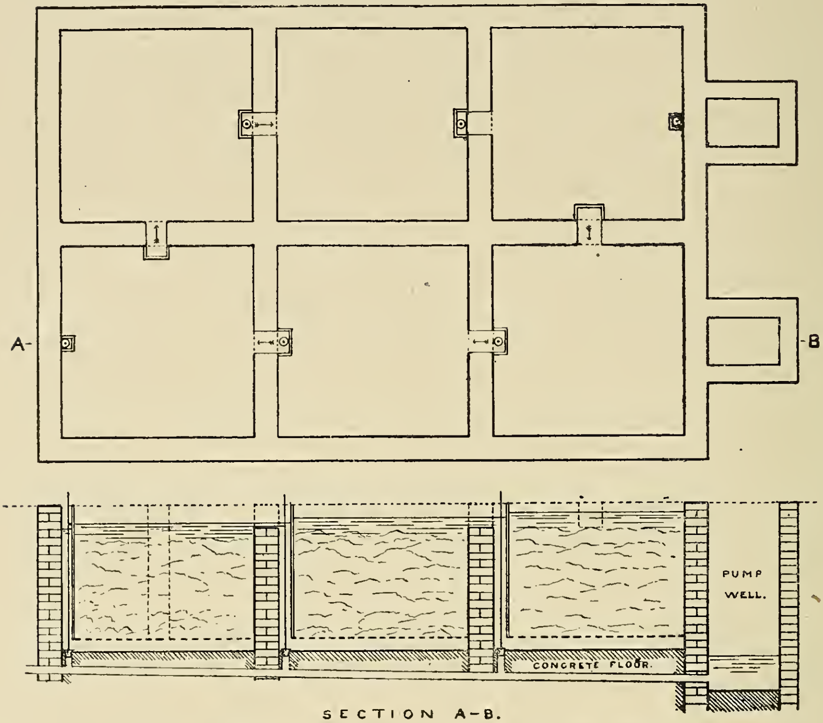

FIG. 90.—Plan and Section of Battery of Press Leaches.

The system of leaches now considered to be the best is based on the continuous circulation of the liquor by gravity from the weakest to the strongest pit. In its different forms the "press leach" is the simplest, and in most cases is all that is required.

A plan and vertical section of the leaches is shown in fig. 90. Assuming that the leaches have been working for some time, and that the liquor in the strongest leach has been run off to the tan-pits, or, in the case of manufacturing extracts, to the decolorising tanks or evaporator, the last vat in the series is now filled with water or spent liquor, which may be heated by steam if desired, and this water, which completes the exhaustion of the material in this vat, forces the liquor forward in the whole series, so that it gets stronger and stronger as it passes from vat to vat. The very weak liquor remaining in the last vat is now pumped into a spare pit, or on to the next stronger vat, pressing the liquor forward as before ; the vat is emptied of the spent material and refilled with new, and now becomes the head leach ; and the strongest liquor is pressed on to it by running water or weak liquor on the weakest vat.

As regards the construction of such a " battery " of leaches, details will differ according to whether the usual English square sunk pits or the American form of circular tub leaches is employed. In the former case the vertical spouts connected with the space under the false bottoms are usually made of wood, like the old-fashioned " eye," and placed at one side or corner of each pit, and connected with the top of the next pit by a short trough, which may be open above or covered as preferred. Both eyes and cross-troughs must be of ample size, so as not to check the running of the liquor, and for a set of six or eight leaches the bottom of the cross-trough should be at least 10 or 12 inches below the actual top of the leach, which should not be filled with material above that level. The object of this is to allow of a sufficient fall from the first to the last leach. Means must be provided for the temporary closing of the cross-trough between the vats which form the first and last leach. On a very small scale this may be done with a plug ; sliding wooden doors are convenient, but difficult to keep tight. A hinged or sliding door held against an indiarubber facing by a wedge or toggle-joint would seem a practicable device.

If round tub leaches are employed, the vertical connection may be similarly made with a wooden trough, but copper tubes are almost essential for the cross connections. If a vertical copper eye in the centre of the leach be provided for boiling or for emptying the leach (p. 398), it may be utilised for the upflow by connecting it with the cross pipe with a thin copper pipe of large diameter, which must be movable for the purpose of casting the leach. A joint like that of a stove-pipe will probably prove sufficiently tight, but if necessary may be made tighter by rolling an indiarubber ring over it.

Six to eight leaches is generally a sufficient number to form a press leach " battery." If more are connected in one series it will usually be necessary to assist the circulation, either by pumping an intermediate leach, or by one or more pumps on the Holbrook system, in which a power-driven pump of simple construction is fitted in the eye of the leach. A simple square plunger in a square " eye " with two hinged flaps is all that is needed, and no bottom valve is required, as the lift is only a few inches. Such a pump will also serve many purposes of agitation and mixing. It is hardly necessary to note that the liquor must run *downward* through the leaches and *up* through the vertical pipes in order to prevent mixture of the weaker with the stronger liquor. This will be rendered the more certain if only the tail leaches are heated, as the *warm* weak liquor will always float on the top of the cold.

Several additions and modifications to the system have been made with a view of obviating the so-called " channel difficulty." There has been a fear on the part of some tanners that the liquid in the leaches may push the material aside and form channels through it, thus preventing proper extraction of the tanning matter. In the Author's opinion this evil has been greatly exaggerated, as, unless the liquid be pumped from the leaches at a very rapid rate while they are in circulation, it is not at all easy for the formation of such channels to take place. In any case it can be entirely avoided by turning over the material in the leaches occasionally, so as to lighten it somewhat and rearrange it a little.

It may also be pointed out that the provision of a proper system for pressing or circulating leaches does not prevent their being pumped off as frequently as desired, though this is generally to be avoided, since when the leach is emptied of liquor the material tends to settle into a compact mass, which is not easy to percolate, and which is liable to shrink from the sides of the pit, thus causing the very trouble which it is desired to avoid. In this case, stirring the material with a pole and running the leach *backwards* for a few minutes will sometimes get over the difficulty by lifting the material. There are some advantages in taking the first and strongest liquors off the material in a separate tank, and then finishing the exhaustion in the press leaches, since many materials swell, and pack tightly when they are first wetted, but on the whole the method hardly pays for its added cost, unless it can be done mechanically. On the larger scale, the automatic extractor mentioned on p. 392 would seem worth consideration, and could be arranged with a chain-conveyor to deliver the wet and swollen material to the required leach.

The press leach system as above described is well adapted for the requirements of tanners, as its first cost is very small in addition to that of the construction of the leaches themselves ; it extracts the bark well, and saves much labour in pumping, and greatly lessens the tendency of the pumper to miss pits in the series to save time when the master's eye is not on him. Another advantage which is often important, is that when the leaches are full, much more than a single liquor can be run from the head leach without pumping on; and similarly when they are run down to their lowest level, much more than a single liquor can be pumped on to the worst leach before it overflows. As the leaches flow slowly in comparison to the rate at which liquors can be pumped by a good steam pump, it is very advantageous to allow the pump to discharge into a liquor-tank raised to such a height that the liquor can be run from it into any leach at a suitable rate for the circulation, and it also enables liquors to be pumped without waiting till room has been found for them in the leaches. Similar tanks are very useful in running liquors for the yard, and especially for the suspenders in a sole leather yard, enabling circulation to be kept up during the night and at other times when the pumps are not running. They may also be used as filters for the suspender liquors by fitting them with false bottoms covered with a layer of nearly spent tan. The liquors may be distributed to the different pits and leaches by means of canvas hose-pipes, or, what is often more convenient, by overhead troughs, carefully levelled, and fitted with discharge valves where required. The latter are conveniently made of lead in a hemispherical form,[1] resting on an indiarubber washer supported by a light brass casting, or a suitably turned rebate in a block of wood (*cp.* p. 550 and fig. 91). Such valves, if good indiarubber is used, wear well, and are absolutely tight.

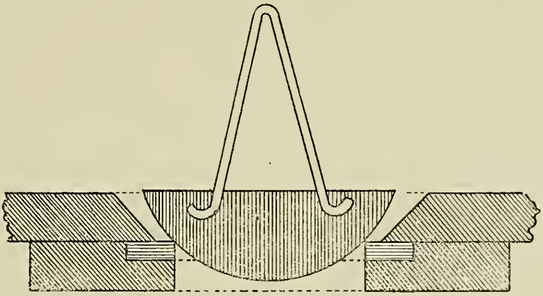

Fig. 91.—Valve for Liquor Troughs.

In England leaches are usually sunk in the ground, and are

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[1] The lead can be cast in a suitably shaped pressed-steel basin, black-leaded to prevent its adhesion, and with the wire link suspended in it.

frequently made of brick and cement, or of large Yorkshire flagstones. Such leaches are somewhat costly, but very durable. Square wooden pits, puddled outside with clay, are also used, and last well with cold, or even warm, liquors, but will not stand direct steaming, the wood gradually bending and allowing the clay to leak into the liquor, causing black stains. On the construction of vats with reinforced concrete compare p. 549. The large round vats of thick pine, and often holding 10 or 12 tons, which are generally used in the United States, stand boiling much better, and are frequently supported above a tramway or conveyor, into which the spent bark can be discharged through a manhole in the bottom. If this method is adopted, it must be remembered that bark, and indeed most other tanning materials, will not run through a hole like corn, but must be cast into it, so that unless the vat is of great depth it is simpler, and almost as easy, to cast over the top. If the manhole is used, either the manhole must be almost the size of the pit, or a central hole must be made in the false bottom, and this must be surmounted by a copper pipe made in sections of 2 or 3 feet, and reaching to the top of the leach. When the pit is to be emptied, the top length is removed, and the tan shovelled down the hole until the second length is reached, and the process repeated. The central pipe serves also for the circulation of the liquor when the pits are boiled, and may be used as the ascending pipe for circulating on the press leach system. It is simply jointed like a stove-pipe.

In the United States several machines have been introduced for the mechanical casting of leaches, one of which is shown in fig. 92. The writer has no experience of their efficiency, but their use seems to be practicable, and would obviate one of the most laborious and unpleasant operations of the tannery. That illustrated is made by the Chas. H. Stehling Co. of Milwaukee, Wis., but a very similar machine is constructed by the Carley Heater Co., Olean, N.Y., and both firms supply brass pitch-holes and other necessary parts. The mode of operation will be clear from the illustration, the rotating shover being lowered into the leach as the pitching proceeds. The same machine can be used for evenly spreading the material as the leach is being filled, and of course can be shifted from one leach to another as required. The pitch-hole is near the side of the leach, and Messrs Stehling inform me that it is easily kept open by the insertion of a conical plug during the leaching, which is withdrawn for pitching, any slight subsequent choking being easily cleared. The leach must of course be a round one, but may be constructed of timber or reinforced concrete, the latter being recommended by Messrs Stehling.

Leaches even up to 20 feet diameter can be pitched, but in the opinion of the present writer 8 feet is a quite large enough diameter, and it is better to multiply the number of leaches than to make them excessively large. It is also undesirable to make them extremely deep, as the tendency is to compress the material and make circulation difficult.

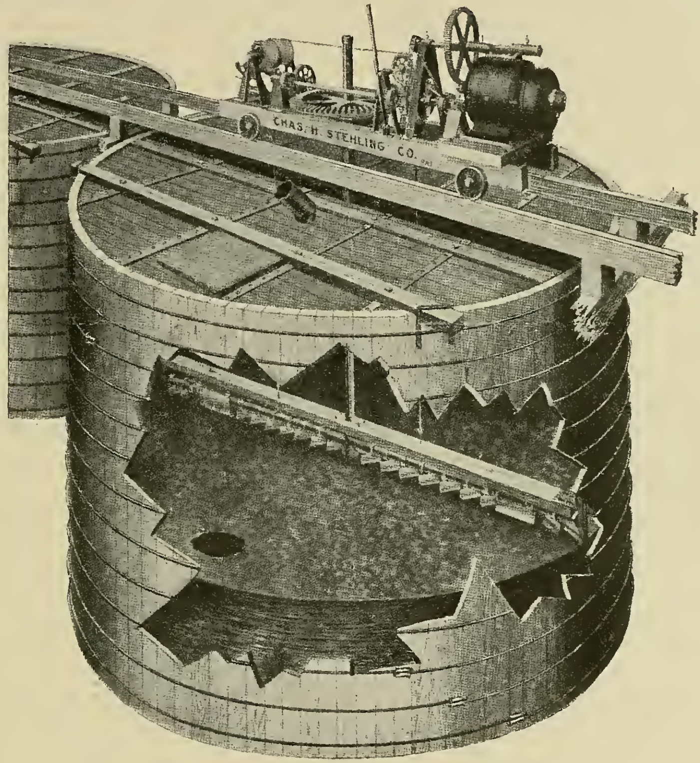


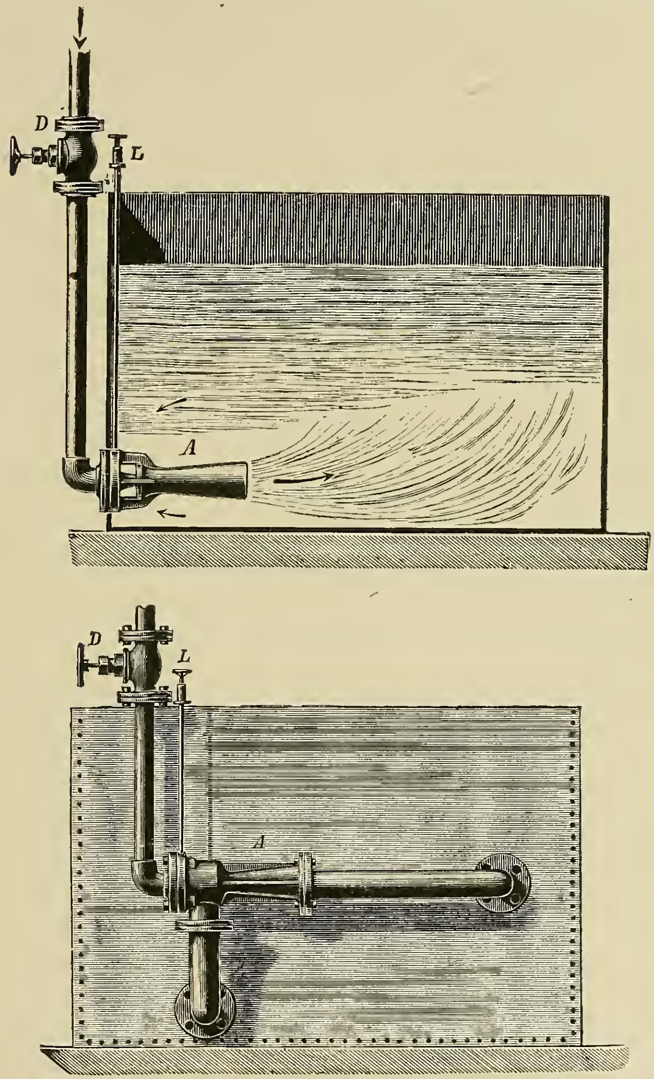
FIG. 92.—Leach Casting Machine.

The question of the influence of temperature on extraction is discussed on p. 412, but except where a pale colour is all-important, it is generally profitable to use a moderate degree of heat in extraction. In the opinion of the writer (which is supported by a vast amount of careful experiment) only the nearly exhausted leaches should be heated, not merely to avoid discoloration, but to extract the maximum amount of tannin. In extract manufacture, where a large quantity of material has to be extracted in a short time in a limited number of leaches, and where the obtaining of strong liquors is more important than the greatest economy of material, much more boiling must often be resorted to, and steam coils are better than open steam. In American tanneries the boiling is frequently done by copper coils fixed below the false bottoms of the vats, but such coils are very costly, and, where weak liquors only are to be heated, seem to present no advantage over a well-arranged system of heating by direct steam, in which care is taken that dry steam only is used, and that all water condensed in steam-pipes, and usually containing iron, is removed by effective steam-traps. If steam is blown into cold liquor through an open pipe a very disagreeable rattling and vibration is produced, which is not only annoying, but is very injurious to the leaches. This evil may be avoided by the use of " silent boiling jets " on the principle of the steam-jet water-raiser ; and, following a suggestion of the writer, these jets may be used at the same time to circulate the water through the tanning material of the nearly exhausted vat, and so wash out the last traces of tan. The simplest way to accomplish this is to lower the boiling jet, directed upwards, and connected with a movable steam-pipe, into the eye of the leach (which is preferably central) so that the heated water flows over its top and percolates downwards through the material to be washed. Two forms of these boiling and mixing jets made by Messrs Körting are shown in figs. 93 and 94, and similar jets are now also made by English engineers.

Batteries of closed copper extractors, worked on the press system, and similar to those used in extracting sugar from beetroot, have frequently been advocated, but are very costly, and have no other advantage for tanners over open vats than that the liquor can be forced through the series by pressure instead of circulating by gravity. No advantage is gained by boiling under pressure, since even boiling in open vats has been shown to destroy tannin, darken the colour of the liquor, and increase the amount of insolubles, and higher temperatures are still more injurious.

Closed vats worked at pressure are, however, much used by extract manufacturers, as they certainly enable a higher gravity extract to be made from the same weight of material, principally by bringing certain woody constituents into solution which are not dissolved at lower temperatures. Such extracts frequently give the reaction for lignin which is usually characteristic of sulphite-cellulose liquors.

Similar objections would not apply to working such extractors at so high a vacuum as would cause the materials to boil at a low temperature. The boiling would expel liquid from the pores,

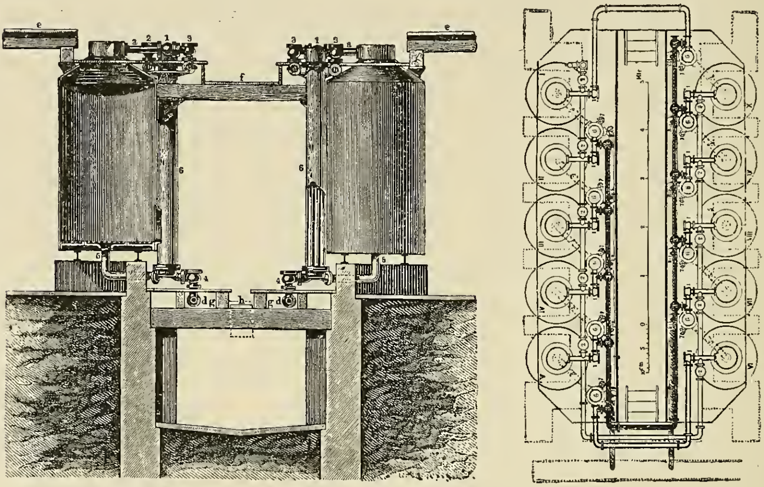


Figs. 93 and 94.—Boiling and Mixing Jets.

which would again be filled with fresh liquor on reducing the vacuum, and this would probably lead to very rapid and complete extraction, while all necessary moving of liquors would be just as well done by the atmospheric pressure as by steam pressure in excess. Where airtight extractors are available, the method seems well worth trying.

Figs. 95 and 96 show a battery of extractors such as are used in the manufacture of beetroot sugar. To adapt them for use in tannin extraction it would probably be desirable to enlarge the discharging manholes, perhaps to the whole diameter of the autoclave.

Heating the weakest leach in the press leach system promotes the even circulation of the liquor, since the warm weak liquor is much lighter than the colder and stronger liquors in the forward leaches, and so floats on the top, and presses the stronger liquor uniformly downwards. It also has the advantage that the liquors are cooled before they are strong enough for the yard, while in tanneries where all the leaches are heated expensive tubular coolers are often employed. As the liquor cools, much of the colouring matters and reds dissolved in the hot liquor separate, and are filtered out by the tanning material, so that much brighter and lighter-coloured liquors are obtained.



Figs. 95 and 96.—Battery of Sugar Extractors.

Sprinkler Leaches (fig. 97) were formerly used in many tanneries and extract factories, especially in the United States. They were introduced by Allen and Warren, and yield a liquor which is at first very strong, but which becomes very rapidly weaker as the running is continued. These leaches are similar in principle to the mashing-tub and sparger of the brewer, but the process is not well adapted for tanners' use, as the material is left too much exposed to the air, which is apt to cause oxidation and loss of tannin. It is also extremely difficult to completely exhaust the material without using an impracticably large volume of water. Sprinkler leaches are arranged so as to spray the liquor, or water, on to the top of the solid material which is to be extracted at such a rate that it flows out just as rapidly as it flows into the vat. Some idea of the great amount of oxidation and consequent loss of tannin which takes place in this form of extractor may be obtained when it is remembered that this same method is now used for the destruction of sewage matter by spraying it on to beds of coke so that it may be mixed with as much air as possible before it is attacked by the bacteria of the coke-beds (see p. 568), and also to oxidise weak alcohol to acetic acid in the "quick vinegar process."

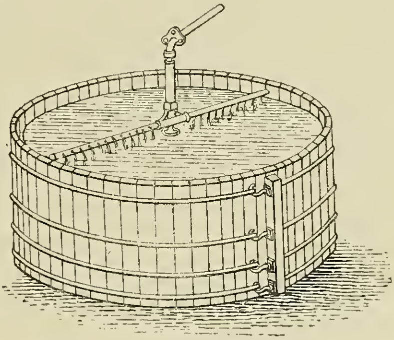


FIG. 97.—Sprinkler-Leach.

So far as extraction is concerned, there is no difference in principle between the methods adopted by the tanner and the extract manufacturer, though the latter usually works on a larger scale, and not unfrequently, in order to increase his output or the gravity of his extract, employs a higher temperature. This is probably justified by practical considerations in the manufacture of extracts from very low-grade materials such as oakwood, which only contains 2 to 3 per cent. of tanning matter, or even of chestnut wood which is somewhat stronger, but it is one of the causes why decoloration of the battery liquor is generally necessary.

Liquors which have been extracted at high temperatures almost invariably require decolorisation by the addition of some substance which precipitates a small proportion of tannin, but carries down with it much of the colouring matter, and of the colloidally suspended "difficultly soluble" tannins. The principle is quite the same as that of the cook clearing her jelly with white-of-egg.

Dried blood, so-called "blood crystals," is chiefly used as the decolorising agent, but a paste of blood-albumen has been placed on the market, which is said to be free from several of the disadvantages attending the use of the crude material.

The liquor to be decolorised is run into a mixing vat fitted with a steam coil capable of raising the temperature of the liquid to at least 80° C., and usually provided with a simple rotary stirring gear. The liquor, as run into the mixing vat, must not have a temperature of more than 48° C. (118° F.) nor a strength of more than about 20° Bkr. (sp. gr. 1·020).

The blood or albumen dissolved in a little water is added to the contents of the vat, which are then well mixed, and the temperature is raised to over 70° C., when the albumen coagulates and carries down much of the colouring matter. The solution is run into another tank, where the precipitate is allowed to settle, and the clear liquor is then drawn off for the evaporation. The muddy portion, about 8 inches in depth, is pumped through filter-presses (which may be cheaply constructed of wood), the clear liquors going to the evaporators, and the press-cakes being dried for manure.

In addition to blood-albumen, several other substances, such as lead acetate (sugar of lead), salts of alumina, alkaline solutions of casein and other albuminous matters, and crushed oil-seeds have been employed in the decoloration of extracts, but they are by no means so efficient as albumen.

Decolorising always causes a loss of tanning matter, some of this being carried down with the precipitated colouring matter, and is for this reason to be dispensed with whenever its use is not really necessary. It may often be avoided by careful extraction at moderate temperatures, and this is especially to be aimed at in the case of strong tanning materials, which easily yield battery liquors of much greater strength than 20° Bkr., and which thus, if they can be sent direct to the evaporator, save cost in evaporation, which is often an important consideration.

Another method which is frequently used to brighten the colour of extracts is treatment with sulphurous acid. Dilute sulphurous acid solution may be used for extraction, but a more common method is to pass sulphur dioxide gas into the liquor before concentration. Sulphurous acid acts partly as a weak acid in decomposing compounds of the tannins and colouring matters with bases, such as lime, iron, copper, but more actively by reducing oxygen compounds and preventing oxidation. Bleaching in this way does not actually destroy or remove the colouring matters, which are apt to reappear on exposure to the air, either in the liquor, or perhaps more often in the leather tanned with it, so that the gain is frequently more apparent than real. If present in any considerable quantities, sulphurous acid may also cause inconvenience by its swelling action on the pelt, and also by attacking the evaporator, but is mostly expelled in concentration.

Another process should perhaps also be mentioned here, though not strictly a means of bleaching. Several tanning materials, and notably quebracho and hemlock, contain large quantities of "difficultly soluble tannins," which render the liquors made from their extracts turbid on cooling. These tannins form soluble compounds with alkalies and with alkaline sulphites, in the latter case probably setting free the sulphurous acid and combining with the base. This has been taken advantage of in a patent [1] in which quebracho and other extracts are rendered soluble by heating in closed vessels with bisulphites, sulphites, sulphides, or even caustic alkalies, and many "soluble quebracho extracts" made on this principle are now on the market. In this case, even where bisulphites are used, the greater part of the sulphurous acid, after serving its purpose in preventing oxidation, escapes in course of manufacture, and the extracts may remain neutral or alkaline, but as they are largely used as "bleaching" extracts, the presence of SO_2 is mostly desired. There is no reason that such extracts should not prove serviceable in tanning, but it has recently been shown by Paessler that the alkaline tannin is not absorbed by neutral hide-powder, and it therefore may lead not only to discrepancies in analysis, but, in case of drum-tannage, where no acid is naturally present, to failure to utilise the whole of the tannin, though, when added to ordinary liquors, the acids contained in the latter will set free the tannins. Dr Lepetit has shown that quite radical changes are produced in the tannin of quebracho by autoclave treatment with bisulphites.

A satisfactory soluble quebracho extract has been made in Germany by treatment with sodium carbonate, and subsequent slight acidification with a weak acid.

The use of ferrocyanides has been suggested as a means of precipitating iron and copper present in extracts, and it may also be pointed out, that with many red-coloured tanning materials, such as hemlock and quebracho, the addition of small quantities of alum to the tanning liquor effects considerable improvement in colour, not only by precipitating a part of the difficultly soluble "reds," but by developing the yellow colour of certain colouring matters (quercetin, myricetin, etc.) which may be present. Such

[1] Lepetit, Dollfus, and Gansser, Eng. Pat. 8582, 1896.

an addition does no harm in the case of soft leathers, but would probably be injurious in a sole leather tannage.

The liquors, whether direct from the leaches or from the decolorising vats, must be concentrated by evaporation to syrupy consistency for liquid extracts, or until they will become nearly solid on cooling, if a solid extract is required. As has already been stated, the action of heat tends to cause a loss of tannin and a darkening of colour by decomposition and the formation of insoluble reds. To reduce this loss to a minimum the weak liquors are evaporated with as little access of air and at as low a temperature as possible, and these conditions are best obtained by the use of steam-heated vacuum evaporators.

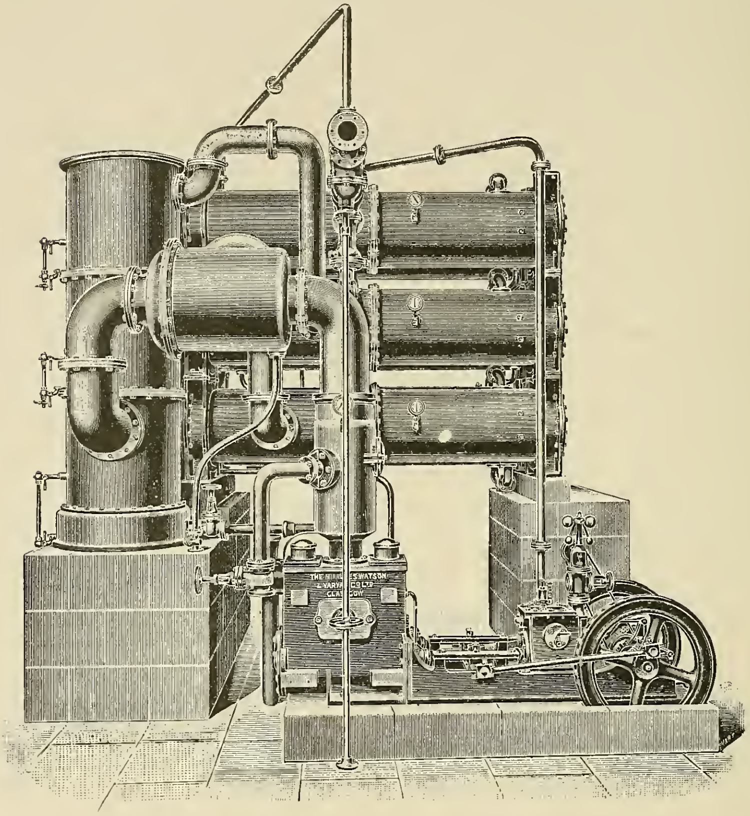


Fig. 98.

It has been explained in Chapter IX. that the boiling temperature of a liquid is simply that at which the vapour-pressure is able to form bubbles in the interior of the liquid, and that it therefore may be lowered as much as is desired by reducing the external pressure to which the liquids are subjected. In the vacuum pan the external pressure of the atmosphere is to a large extent removed by means of an air-pump, so that the liquid

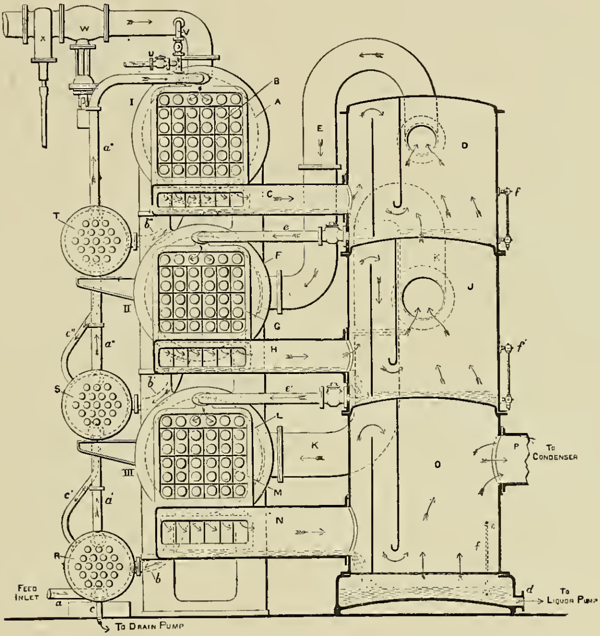


FIG. 99.

may boil freely at very low temperatures, and, consequently, with little injury to the liquid by heat. Although the boiling temperature is reduced in this way, the actual *quantity* of heat required for evaporation is not lessened, and if heat is not supplied from outside, water may actually be frozen by the cooling caused by evaporation *in vacuo*, and practically as much steam is required to evaporate a quantity of water in the vacuum as in an open pan. This quantity, and the consequent consumption of fuel, can, however, be much lessened in vacuum apparatus by what is known as multiple "*effets*," or effects. If we imagine a liquid boiling by steam or open fire at atmospheric pressure it is producing steam at 100° C., and this steam can be employed to boil liquid in a pan where the boiling point is reduced by vacuum to say 90°, and the steam from this again to boil one with still higher vacuum and lower boiling point, the heat of evaporation in the first pan being recovered in the succeeding one by again condensing the steam to water, when as much heat is liberated as was before consumed. Thus in a single-effect evaporator 1 lb. of coal burnt under the boiler may evaporate 8½ lb. of water, in a double-effect 16 lb., in a triple 23½ lb., and so on, some loss being incurred by waste of heat at each effect, till there comes a point when the saving of fuel will not repay for the prime cost and wear and tear of the apparatus, and it is rarely worth while to go beyond three or four effects. Each case must be judged on its merits, and in some cases a single effect is commercially the most economical.

As regards the detail of the pan, the oldest form, used in sugar concentration, was merely a steam-jacketed pan with a copper dome, from which the escaping steam was carried to a condenser and then to an air-pump. As the boiling was violent and much spray was produced which carried over sugar, it was found necessary to introduce a spray-separator between the pan and the condenser. In more modern pans the heating is often done by a steam-box inside the pan with vertical tubes so as to expose a larger surface, and cause a quicker circulation.

To a considerable extent these forms of pan have been superseded by apparatus in which the liquid is sprayed through tubes heated externally by steam, the boiling being almost instantaneous, and the liquid being evaporated and carried through the apparatus in five or six minutes, during which it is never exposed to an ordinary boiling temperature. Perhaps the earliest, and still one of the best, of these machines is the Yaryan,[1] which is shown in fig. 98, and its internal construction in fig. 99. In this machine the tubes are horizontal. In the Kestner [2] "Climbing Film" evaporator they are vertical, and the liquid is carried up in a thin film on the sides of the tubes by the escaping steam, and the evaporated liquid is delivered at a considerable height, which is sometimes advantageous; or the evaporation may be carried further in a "Falling film" body. These evaporators can of course be combined to multiple effects. Several of them are in successful use in British tanneries, where they were in the first instance installed to concentrate partially exhausted liquors, but in some cases are now used for the manufacture of fresh extract from mimosa bark and other materials. Single- and

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[1] Mirrlees, Watson & Yaryan, Glasgow.

[2] Kestner Evaporator and Engineering Co., Ltd., 37 Parliament Street, Westminster, S.W. 1.

triple-effect climbing film evaporators are shown in figs. 100 and 101. In some cases the exposure to heat is so short that the evaporator is satisfactorily worked at ordinary boiling temperature without vacuum, as no perceptible injury is caused to the liquor.

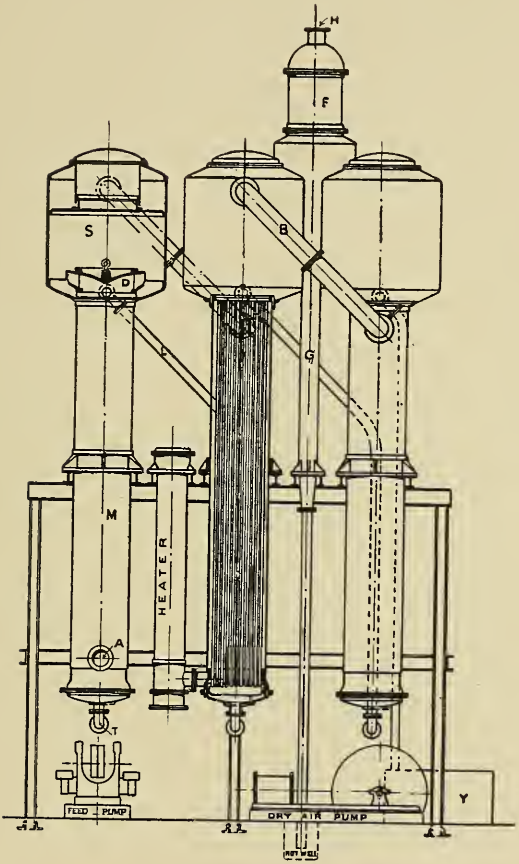

FIG. 100.—Triple effect.

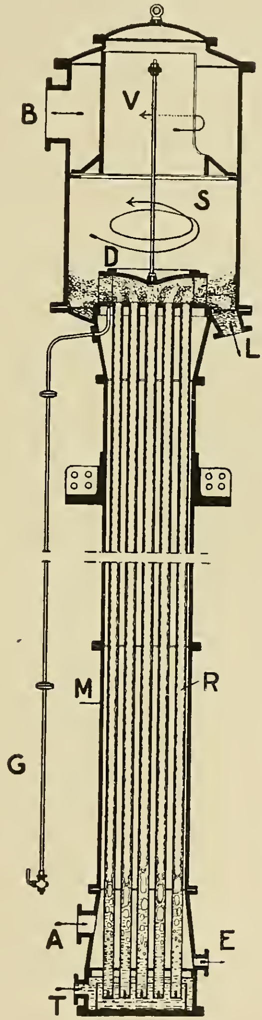

FIG. 101.—Single effect.

Somewhat similar appliances, the "Simplex" and "Multiplex" evaporators, are made by Messrs Blair, Campbell & M'Lean Ltd. (Govan, Glasgow), and the latter is shown in fig. 102.

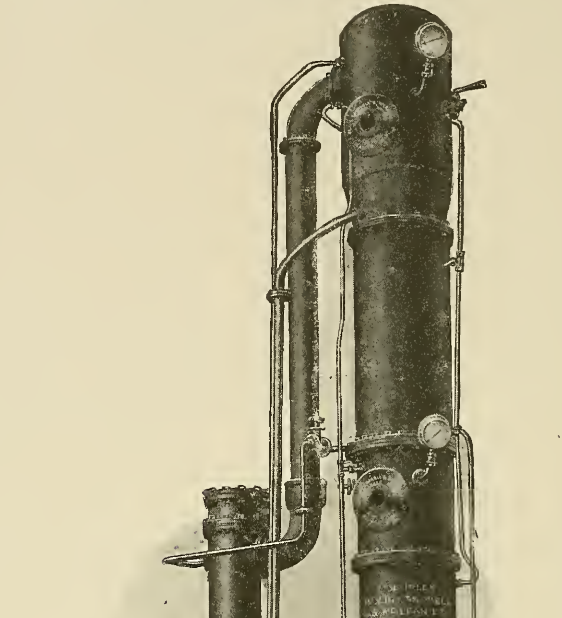

Fig. 102.

In the evaporation of very viscous liquids, as, for instance, in the manufacture of solid extracts, these appliances are found unsuitable for the final evaporation, as the tubes are liable to choke, and modified forms of the simple pan are adopted, often fitted with stirrers.

As many tanning materials contain small quantities of acetic and other volatile acids, it is found necessary in multiple effects to have not only the tubes but the outer steam casings made of copper to avoid corrosion,[1] but in single effects this trouble does not occur. In single effects worked at atmospheric pressure the steam from the evaporating liquid may often be used for heating purposes with great economy. Where vacuum is adopted, the exhaust steam from the vacuum engine is frequently used for heating the first effect.

In the case of a solid extract, the evaporation must be carried on until it is as thick as can be run from the apparatus. To do this satisfactorily, stirrers must be provided to keep the extract in motion so long as it is in the pan. The thick, hot liquid extract is then run into boxes lined with paper or other suitable material, where it is allowed to cool and to solidify.

The pan for the final evaporation of solid extracts should be planned so as to allow of easy cleaning and ready access to its interior, so that if accidentally the evaporation is carried so far that the liquid will not run out, the clearing of the pan may be a comparatively easy matter. It is also important that the extract exit should be of large size. Probably a broad and somewhat shallow pan, heated merely by a steam jacket, and fitted with rotating stirrers, is the most suitable.

The Use of Extracts in the Tannery.—One of the great attractions of extracts is that they save the trouble and cost of leaching, and as the extract manufacturer makes this his specialty, he can often extract more tanning matter from a material than the tanner who has no means of concentrating his weak liquors. The extract manufacturer also can employ methods of decoloration which would be impracticable to the tanner, and so enable the latter to obtain better colour than if he employed the raw material. By the use of extracts a tanner can strengthen weak liquors without trouble, and with definite quantities of materials ; and by using extracts for this purpose he is enabled to use up the weaker liquors of his leaches, and so employ more water and obtain better extraction of his solid materials than if he used them alone. In the case of very weak materials like oakwood, the difficulties of making liquors of sufficient strength for tanning without evaporation are so great as to render such

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[1] It is very probable that some of the modern acid-resisting forms of cast iron might be used.

materials useless to the tanner for his own extraction, and their carriage even for short distances may amount to more than their total value. Even with much richer materials extraction effects a saving if the carriage is a long one, as it rarely pays to import any material containing less than about 25 per cent. of tanning matter. Even when the strength of the natural material is considerable, as in the case of quebracho, extraction may be profitable if from its hardness, or other reasons, the material is difficult for the tanner to handle. For long voyages, and especially from the tropics, solid extracts are more suitable than liquid, as the expense of casks is saved, and the danger of fermentation is lessened. As it is impossible for the tanner to judge by appearance or consistency of the strength or value of extracts, they should always be bought and sold on the analysis of the particular shipment or parcel by a competent chemist. For directions for sampling see Chapter XX.

Extracts simply require to be dissolved in a suitable quantity of water or weak liquor at an appropriate temperature to obtain a liquor of any required strength. Some extracts are completely soluble in cold water or liquor, but most dissolve better by the aid of heat. 40° to 60° C. (100° to 140° F.) is generally sufficient, and probably no advantage can arise from temperatures over 80° (180° F.). Boiling should be avoided, as it facilitates the formation of insoluble " reds," with consequent loss of tanning matter and darkening of colour. The extract should be run into the vat in a thin stream, and continuously plunged up ; where large quantities of extract are to be dissolved, a mechanical agitator is advantageous. A " silent boiling jet " (p. 401) may be used, fitted into a small casing immersed in the liquor and open at both ends, and the extract run into the current it produces.

Whether in the manufacture of extracts or for direct use in the tannery, the temperature at which tanning materials are extracted is of prime importance. It is a common mistake to assume that the largest amount of tannin is extracted by boiling. Mr A. N. Palmer has pointed out that this is by no means the case, but that each material has an *optimum* temperature of extraction, at which more tannin is extracted than at any other, though a small additional amount can be obtained by boiling the extracted residue. The method adopted in analysis of extracting as much as possible at low temperatures, and only raising to boiling point when half the required volume of liquor has been obtained, is intended to give a maximum extraction of materials for which the *optimum* point is not known, and is a good principle to follow in practical leaching. The question has been carefully investigated by J. G. Parker and the Author,[1] with results which are given in the following tables. For many purposes the colouring matter which accompanies the tannin is a serious disadvantage, and it is usually mostly extracted at the higher temperatures, and on this account it is necessary for the tanner who will work his leaches economically to ascertain at what temperature he can extract the largest amount of tannin combined with no more colouring matter than he can permit to enter his leather. Most materials are satisfactorily extracted at 50° to 60° C., but as a general rule it is best to begin cold or nearly so, and only raise the temperature as the extraction proceeds. The tables show the percentages of tanning matter, and the amount of colour (as measured by Lovibond's tintometer), obtained by extracting materials in a Procter's extractor (*L.I.L.B.*, p. 102, *L.C.P.B.*, p. 94) so long as any colour or tannin could be obtained.

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[1] *Journ. Soc. Chem. Ind.*, 1895, 635.

BELGIAN OAK BARK

Temperature of Extraction.	Tanning Matters absorbed by Hide.	Soluble Non-tanning Matters.	Per cent. of Tannin on Maximum Yield.	Colour of ½ per cent. Solution in ½-inch Cell. Red.	Colour of ½ per cent. Solution in ½-inch Cell. Yellow.	Per cent. of Colour on Maximum Yield.
° C.	Per cent.	Per cent.		Deg.	Deg.	
15	5·9	5·1	61·9	8·6	23·1	57·4
15–30	6·8	5·5	70·7	9·2	26·4	64·5
30–40	8·0	5·5	83·5	11·6	30·4	76·1
40–50	8·2	5·7	84·2	12·0	32·1	80·0
50–60	8·5	5·8	87·6	12·5	36·0	84·0
60–70	9·1	5·9	95·5	13·1	38·1	92·7
70–80	9·2	6·0	95·7	14·7	38·9	98·7
80–90	9·6	6·0	100·0	14·0	36·9	93·2
90–100	9·6	6·1	100·0	14·0	41·2	94·6
Boiled ½ hour	9·1	6·6	93·7	15·0	42·6	100·0

MYROBALANS

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum Yield.	Colour of $\frac{1}{2}$ per cent. Solution in $\frac{1}{2}$-inch Cell.		Per cent. of Colour on Maximum Yield.
				Red.	Yellow.	
° C.	Per cent.	Per cent.		Deg.	Deg.	
15	28·5	12·8	79·2	1·09	4·9	97·4
15–30	30·1	13·6	83·6	1·00	4·1	82·5
30–40	32·3	14·3	89·8	1·03	4·1	82·7
40–50	33·5	13·6	93·0	1·03	4·2	84·4
50–60	34·7	14·4	96·4	1·03	4·4	87·6
60–70	34·8	14·4	96·6	1·03	4·5	89·3
70–80	34·9	14·9	96·8	1·10	4·7	94·1
80–90	35·1	15·0	97·4	1·16	4·8	96·7
90–100	36·0	14·9	100·0	1·12	4·9	97·0
Boiled	35·4	15·5	98·1	1·26	4·9	100·0

Smyrna Valonea

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum Yield.	Colour of ½ per cent. Solution in ½-inch Cell.			Per cent. of Colour on Maximum.
				Red.	Yellow.	Blue.	
° C.	Per cent.	Per cent.		Deg.	Deg.	Deg.	
15	25·5	19·1	70·5	2·5	6·0	0·3	74·6
15–30	29·1	18·3	74·5	2·5	6·4	0·3	78·0
30–40	33·6	18·1	86·2	2·3	6·4	0·3	76·2
40–50	35·5	18·1	86·2	2·3	6·5	0·3	74·6
50–60	39·1	16·6	100·0	2·0	6·0	0·3	76·2
60–70	38·6	17·0	99·0	2·0	6·8	0·3	84·7
70–80	38·8	17·5	99·5	2·1	7·4	0·4	84·7
80–90	36·9	17·2	95·0	2·2	7·6	0·4	84·7
90–100	36·6	17·0	94·0	2·4	7·8	0·5	90·6
Boiled	35·4	17·6	90·6	3·0	8·2	0·6	100·0

GREEK VALONEA

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum Yield.	Colour of ½ per cent. Solution in ½-inch Cell.			Per cent. of Colour in ½ per cent. of Tannin Solution.
				Red.	Yellow.	Blue.	
° C.	Per cent.	Per cent.		Deg.	Deg.	Deg.	
15	16·0	13·0	64·0	2·9	6·3	0·3	67·3
15–30	18·1	12·6	72·4	3·0	6·6	0·3	70·0
30–40	21·1	12·0	84·4	2·8	6·5	0·3	68·0
40–50	23·6	12·1	94·4	2·4	6·6	0·3	65·9
50–60	24·8	12·4	99·2	2·7	7·0	0·4	71·6
60–70	25·0	12·6	100·0	2·9	7·3	0·5	75·8
70–80	24·6	12·5	98·4	3·1	7·9	0·6	82·3
80–90	24·0	12·5	96·0	3·4	8·1	0·6	85·8
90–100	23·6	12·6	94·4	3·5	8·8	0·7	92·0
Boiled	22·6	13·0	88·8	3·9	9·4	0·8	100·0

NATAL MIMOSA

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum.	Colour of ½ per cent. Solution in ½-inch Cell.		Per cent. of Colour on Maximum.
				Red.	Yellow.	
° C.	Per cent.	Per cent.		Deg.	Deg.	
15	21·2	11·6	66·2	2·6	4·1	51·1
15–30	29·0	9·8	90·6	3·0	4·1	54·2
30–40	30·1	9·8	94·0	3·0	4·4	56·5
40–50	30·2	9·8	94·4	3·1	5·0	61·8
50–60	30·4	10·4	95·0	3·9	6·5	79·9
60–70	31·5	10·6	98·4	4·2	6·5	81·6
70–80	32·0	10·8	100·0	4·2	7·0	85·5
80–90	30·8	11·2	96·2	4·9	7·4	93·8
90–100	30·1	11·8	94·0	5·3	7·8	100·0
Boiled	29·4	12·0	91·8	5·7	7·2	98·4

SUMACH

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum.	Colour of ½ per cent. Solution in ½-inch Cell.		Per cent. of Colour on Maximum.
				Red.	Yellow.	
° C.	Per cent.	Per cent.		Deg.	Deg.	
15	14·2	17·8	70·0	1·6	5·4	63·6
15–30	17·6	18·1	86·7	1·4	4·3	51·8
30–40	18·5	18·1	91·1	1·3	4·4	51·8
40–50	20·1	18·5	99·0	1·4	4·4	52·9
50–60	20·3	19·1	100·0	1·5	4·7	56·5
60–70	19·0	19·4	93·6	1·7	5·6	66·6
70–80	18·0	19·9	89·1	1·9	6·2	72·8
80–90	16·9	21·1	83·2	2·3	6·8	82·7
90–100	16·6	22·3	81·7	2·6	7·0	87·7
Boiled	15·2	24·0	74·8	3·3	7·7	100·0

QUEBRACHO WOOD

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum.	Colour of $\frac{1}{2}$ per cent. Solution in $\frac{1}{2}$-inch Cell.		Per cent. of Colour on Maximum.
				Red.	Yellow.	
° C.	Per cent.	Per cent.		Deg.	Deg.	
15	7·6	2·2	35·0	8·9	14·1	71·3
15–30	10·1	2·4	46·5	6·4	10·7	68·7
30–40	11·8	2·4	54·4	5·9	9·6	65·2
40–50	15·1	2·4	69·5	5·3	8·4	60·0
50–60	16·5	2·4	76·0	5·4	8·5	60·4
60–70	17·4	2·4	80·0	5·6	8·2	59·9
70–80	19·1	2·7	88·0	6·4	8·6	67·4
80–90	21·7	3·0	100·0	6·4	9·4	74·3
90–100	19·5	3·0	89·8	6·6	9·8	100·0

MANGROVE BARK (*Ceriops*)

Temperature of Extraction.	Tanning Matters.	Soluble Non-Tannins.	Per cent. of Tannin on Maximum.	Colour of ½ per cent. Solution in ½-inch Cell.		Per cent. of Colour on Maximum.
				Red.	Yellow.	
° C.	Per cent.	Per cent.		Deg.	Deg.	
15	13·0	10·4	61·6	14·2	20·8	64·7
15–30	16·1	10·4	76·3	16·1	21·7	69·8
30–40	17·4	12·5	82·4	15·8	23·0	71·7
40–50	18·5	11·4	87·7	16·5	33·5	73·8
50–60	20·3	10·3	96·2	16·0	23·4	72·8
60–70	20·0	11·4	94·7	17·5	31·2	90·0
70–80	20·4	11·2	96·7	16·5	28·3	82·8
80–90	21·1	10·8	100·0	15·4	24·6	73·8
90–100	20·2	11·4	95·7	23·0	34·1	100·0

CANAIGRE ROOT (three years old)

Temperature of Extraction.	Tanning Matters absorbed by Hide.	Soluble Non-Tanning Matters.	Per cent. of Tannin on Maximum Yield.	Colour of $\frac{1}{2}$ per cent. Solution in $\frac{1}{2}$-inch Cell.			Per cent. of Colour on Maximum.
				Red.	Yellow.	Total.	
° C.	Per cent.	Per cent.		Deg.	Deg.	Deg.	
15	21·1	13·0	78·7	1·6	4·1	5·7	41·5
15–30	26·2	12·5	85·6	1·6	3·8	4·4	38·0
30–40	28·1	12·5	91·8	1·4	3·7	5·1	35·9
40–50	30·5	13·1	99·6	2·1	4·2	6·3	44·3
50–60	30·6	13·6	100·0	2·4	4·8	7·2	50·7
60–70	27·2	14·1	88·8	2·5	5·0	7·5	52·7
70–80	26·4	14·6	86·2	2·8	6·1	8·9	62·6
80–90	23·2	14·8	75·8	3·1	6·9	10·0	70·4
90–100	22·8	14·8	74·5	4·3	7·4	11·7	82·4
Boiled $\frac{1}{2}$ hour	19·2	12·3	62·7	5·6	8·6	14·2	100·0

CUBE GAMBIER

Temperature of Extraction.	Tanning Matters absorbed by Hide.	Soluble Non-Tanning Matters.	Per cent. of Tannin on Maximum Yield.	Colour of ½ per cent. Solution in ½-inch Cell.			Per cent. of Colour on Maximum.
				Red.	Yellow.	Total.	
° C.	Per cent.	Per cent.		Deg.	Deg.	Deg.	
15	46·8	21·8	78·0	2·5	7·8	10·3	57·2
15–30	48·8	21·0	81·3	1·7	8·0	9·7	54·9
30–40	50·2	22·0	83·7	1·7	8·6	10·3	57·2
40–50	51·9	23·0	86·5	1·7	8·8	10·5	58·3
50–60	51·1	20·3	91·9	1·7	8·9	10·6	58·8
60–70	55·6	20·3	92·7	1·9	9·4	11·3	62·7
70–80	55·7	20·3	92·8	2·2	10·1	12·3	68·3
80–90	55·8	21·2	93·1	2·3	10·6	12·9	71·6
90–100	56·1	22·0	93·3	2·8	11·6	14·4	80·0
Boiled ½ hour	60·0	20·0	100·0	3·2	14·8	18·0	100·0

BLOCK GAMBIER

Temperature of Extraction.	Tanning Matters absorbed by Hide.	Soluble Non-Tanning Matters.	Per cent. of Tannin on Maximum Yield.	Colour of ½ per cent. Solution in ½-inch Cell.			Per cent. of Colour on Maximum.
				Red.	Yellow.	Total.	
°C.	Per cent.	Per cent.		Deg.	Deg.	Deg.	
15	30·1	27·4	50·1	2·6	8·1	10·7	33·5
15–30	34·8	26·2	69·6	2·4	8·0	10·4	34·0
30–40	40·8	27·2	81·6	2·0	9·0	11·0	55·0
40–50	44·8	27·6	89·6	2·4	9·8	12·2	61·0
50–60	46·8	27·8	93·6	2·4	10·1	12·5	62·5
60–70	47·3	27·6	94·6	2·5	10·6	13·1	66·0
70–80	47·4	27·6	94·7	2·8	10·9	13·7	63·5
80–90	47·6	27·3	95·2	3·2	11·6	14·8	74·0
90–100	48·2	27·1	96·4	3·8	12·8	16·6	83·0
Boiled ½ hour	50·2	26·4	100·0	5·0	15·0	20·0	100·0

CHAPTER XXV

FATS, SOAPS, OILS, AND WAXES

Fats and oils constitute a large class of substances, of animal or vegetable origin, which may be solid, pasty, or more or less viscous liquids, but which in the latter case are commonly known as "fixed" or fatty oils, to distinguish them from the volatile or essential oils, which may be distilled without decomposition, and which are the source of most of the odours of plants, and of quite different chemical constitution. The term "oil" is also applied to various products of mineral origin, and especially to those derived from petroleum, on account of their similarity in appearance and physical properties to the fixed oils, though, chemically, they form a very distinct class. The waxes are another group somewhat closely allied to the fats; and there are certain fixed oils, such as sperm oil, which, though very similar in appearance and properties to the fatty oils, are chemically members of the group of waxes.

As it is obvious that there is no chemical distinction between the fats and fatty oils, except that of melting point, it will be convenient to treat them together, especially as what is a solid fat in one climate may be an oil in another. Palm and cocoanut oils are cases in point, as the first is buttery and the second a hard fat in this country, though they are both liquid in tropical climates.

For more detailed information on the chemistry of fats and oils the reader must be referred to the *Leather Industries Laboratory Book*, sect. xviii., to chaps. x. and xi. of the *Leather Chemists' Pocket Book*, or to the larger manuals devoted specially to the subject by Lewkowitsch, Fahrion, and others; but a few general facts must be recapitulated.

The true fats contain carbon, hydrogen, and oxygen, but no nitrogen. They are all salts of glycerin, with organic acids which are generally termed "fatty acids," and which resemble in many of their physical characteristics the fats themselves.[1] Glycerin

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[1] The names of the neutral fats or "glycerides" terminate in "in," those of the free acids in "ic"; thus the fat or oil of oleic acid is olein. It is best to confine the termination "ine" to the commercial products,

is a very weak base, of the nature of an alcohol or sugar, and, consequently, when a fat is heated with a solution of one of the caustic alkalies, the fatty acid combines with the latter, and the glycerin is set free. The salts thus formed are denominated "soaps." The reaction with stearin (glycerin stearate), the principal constituent of hard animal fats, is shown in the following equation:—

$$\begin{array}{ccccccc}
\text{Stearin} & & \begin{array}{c}\text{Sodium}\\ \text{hydrate}\end{array} & & \begin{array}{c}\text{Sodium}\\ \text{stearate}\end{array} & & \text{Glycerin}\\
(C_{17}H_{35}CO\,.\,O)_3C_3H_5 & + & 3NaOH & = & 3C_{17}H_{35}CO\,.\,ONa & + & C_3H_5(OH)_3.\\
890 & & 120 & & 918 & & 92
\end{array}$$

If a soap is treated with an acid stronger than its own, the latter is set free, while the new acid combines with the base. The following equation, for instance, shows the action of hydrochloric acid on the stearic soap:—

$$\begin{array}{ccccccc}
\begin{array}{c}\text{Sodium}\\ \text{stearate}\end{array} & & \begin{array}{c}\text{Hydrochloric}\\ \text{acid}\end{array} & & \text{Stearic acid} & & \begin{array}{c}\text{Sodium}\\ \text{chloride}\end{array}\\
C_{17}H_{35}CO\,.\,ONa & + & HCl & = & C_{17}H_{35}CO\,.\,OH & + & NaCl.\\
306 & & 36{\cdot}5 & & 284 & & 38{\cdot}5\,\text{[1]}
\end{array}$$

If any soap be dissolved in hot water, and sufficient hydrochloric or sulphuric acid added to render the solution acid, the latter will turn first milky, and (if it be kept warm) the fatty acid will finally rise in an oily layer to the surface, which in many cases will harden, as it cools, to a solid mass. The amount of fatty acid in a soap may be roughly determined by weighing 25 grm., dissolving in 50 c.c. of boiling water, and adding excess of acid, allowing the reaction to take place in a graduated cylinder, or a flask with a graduated neck, in a vessel of boiling water. When the fatty acid has risen to the top its volume may be noted, and each cubic centimetre may be roughly reckoned as 0·9 grm. (For more exact methods *cp.* *L.I.L.B.*, sect. xvii., or *L.C.P.B.*, chap. x.)

Soaps are insoluble in strong caustic alkaline solutions, and therefore saponification (as the decomposition of fats by alkalies

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which are often very different to the pure fats. Thus the "distilled oleine" largely used in wool textiles is mainly free oleic acid together with hydrocarbons analogous to mineral oils, formed by the breaking down of the acid by heat.

[1] It will be noted that the combined weight of the glycerin and the 3 mols. of stearic acid is greater than that of the original stearin by 54, the weight of 3 mols. of combined water.

is called) does not readily take place in them, and for this reason the soap-boiler generally dilutes his caustic soda solutions to a gravity not exceeding 18° Tw. (sp. gr. 1·090), and separates the soap at the end of the operation by the addition of brine, in which it is insoluble. An easier method, and one which is often useful for the preparation of small quantities of special soaps for fat-liquors and the like, is as follows: [1]—10 lb. of a *good* caustic soda, free from common salt, is dissolved in 4 gallons of water, and 75 lb. of oil or fat is warmed to about 25° C. or just sufficiently to render it liquid, and the soda solution is added in a thin stream, with constant stirring, which must be continued until the mass becomes too pasty. It is now set aside in a warm place for at least twenty-four hours, during which saponification gradually takes place. For leather purposes a neutral soap with a slight excess of fat is generally advantageous, so that the fat may be increased to 80 lb.; or, in place of this, the operation will be facilitated by the addition of 5 lb. of commercial oleic acid. If soft soap is desired, 14 lb. of caustic potash may be used in place of the 10 lb. of caustic soda. The hardness or softness of soaps varies to some extent with the fat used, but potash soaps are always much softer than the corresponding soda soaps. It is obvious that with soaps made in this way all the glycerin remains mixed with the soap. If, on testing, the soap does not prove to be free from caustic, it may be re-melted, which will generally complete the reaction. Before attempting to work with large quantities, a laboratory experiment is desirable, using 10 grm. of soda in 40 c.c. of water, and 75 to 80 grm. of oil or fat. The neutrality or freedom of a soap from caustic alkali may be tested by touching a freshly cut surface with an alcoholic solution of phenolphthalein, which the least trace of caustic soda or potash will render pink.

If solutions of soaps are mixed with those of salts of the heavy metals or of the alkaline earths a mutual decomposition takes place, the acid of the salt combining with the alkali of the soap, and the fatty acid with the metallic base, to form a metallic soap. Most of these soaps are sticky masses, insoluble in water, but not unfrequently soluble in turpentine or petroleum spirit if previously thoroughly dried, so that some of them have been applied to the production of varnish. Alumina soaps are occasionally used to thicken mineral oils, or render them more viscous; and soap solutions in reaction with alumina salts are sometimes used to render tannages more resistant to water, and for waterproofing textiles. The general reaction of the stearin

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[1] Carpenter, *Soap, Candles, and Lubricants*, p. 144.

soap with calcium sulphate is shown in the following equation, though in practice it is sometimes more complex :—

$$\overset{\substack{\text{Stearin}\\\text{soap}}}{2C_{17}H_{35}CO\,.\,ONa} + \overset{\substack{\text{Calcium}\\\text{sulphate}}}{CaSO_4} = \overset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \overset{\substack{\text{Calcium}\\\text{stearate}}}{(C_{17}H_{35}CO\,.\,O)_2Ca}$$

This is the reaction which causes the curdling of soap by hard water, and is the basis of the " soap test " (*L.I.L.B.*, p. 30).

True fats cannot be distilled alone without decomposition. When distilled in a current of steam some undecomposed fat passes over, but the greater part is broken up into free fatty acid and glycerin ; and hydrocarbons practically identical with mineral oils are also formed.

Fats and oils are insoluble in water, and in most cases only sparingly soluble in alcohol, but freely soluble in ether, petroleum spirit, benzene, and most other hydrocarbons, as well as in chloroform, carbon tetrachloride, and carbon disulphide. Petroleum spirit, often called benzine, is largely used for their extraction, and for de-greasing leather, and removing grease from clothes. In the laboratory, carbon disulphide or carbon tetrachloride is to be preferred, the latter having the advantage of being non-inflammable. Chloroform has lately been adopted as a fat-solvent in the analysis of leather by the American Leather Chemists' Association. It extracts rather more than petroleum spirit. Castor oil is an exception to the rule. Owing to the large proportion of oxygen which it contains, it is readily soluble in alcohol, and very sparingly in petroleum spirit. Other oils, when oxidised, usually become more soluble in alcohol, and less so in hydrocarbons.

Oils vary much in their tendency to " dry," or become converted into solid or sticky resin-like substances. This tendency is greatest in some of the seed oils, and least in olive oil and the oily part of animal fats (tallow oil, neatsfoot oil). Sperm oil, a " liquid wax," is also very free from this tendency, but all other marine oils possess it in a greater or less degree. It is not due to evaporation, but to the absorption of oxygen by the " unsaturated " fatty acids. The tendency to oxygen-absorption, and consequently to drying (and, in the case of leather-oils, to " spueing "), is measured analytically by the " iodine value," the absorption of iodine (or bromine) being proportional to that of oxygen, while it is much more easily measured.

There are no simple tests by which the purity of oils can be determined, though in a few cases the presence of particular oils can be detected. The colour-reactions which used to be relied on are mostly due, not to the oils themselves, but to natural impurities which can often be removed by treatment. The mixing and adulteration of oils is now a science, and those who practise it are well acquainted with the customary tests, and take care to adjust their mixtures so as to meet them. Taste and smell, with practice, often furnish useful indications, but proper chemical examination is the only safe guide, and since it has become common, adulteration has a good deal diminished.

Natural oils and fats are invariably mixtures of the glycerides of several fatty acids, and their qualities depend simply on the character of these glycerides and the proportions in which they are mixed. The fatty acids form several groups, differing in their degree of "saturation,"[1] or, inversely, in their power of taking up oxygen, on which their tendency to drying depends. The members of any one of these groups resemble each other strongly, differing principally in melting points, density, and other physical characteristics. It is possible for a glyceride to contain two, or even three, *different* fatty acids.

Saturated Fatty Acids.—Stearic acid, $C_{17}H_{35}CO.OH$, and palmitic acid, $C_{15}H_{31}CO.OH$, are the most important. At ordinary temperatures they are hard, white, crystalline bodies, and melt at 69° and 62° C. respectively. They do not, under ordinary circumstances, absorb any oxygen or iodine, and are very little liable to chemical change. Together with oleic acid they are the principal acids of tallow and other animal fats, while palmitic acid and some lower members of the same group are more common in vegetable oils. Free stearic acid is an important constituent of the "distilled stearines" used in currying; while "oleostearine" from pressed tallow consists mainly of the neutral fats or glycerides of stearic and palmitic acids. The glycerides of saturated acids are hard fats.

Liquid Fatty Acids, Non-drying.—Of these, oleic acid is much the most common and important, its glyceride, olein, forming the liquid part of animal fats, and being the principal constituent of vegetable non-drying oils. Olive oil consists almost entirely of olein, with a little palmitin. The formula of oleic acid is $C_{17}H_{33}CO.OH$, thus differing from stearic acid in having two atoms of hydrogen less. The "bonds" or affinities corresponding to these two atoms are linked together, but can separate, and attach two atoms of iodine, bromine, or chlorine, or one of

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[1] A "saturated" compound is one the constituents of which are present in such proportions that all the combining affinities of each are satisfied by the others. Iodine value, see *L.I.L.B.*, p. 176, and *Journ. Soc. Chem. Ind.*, 1902, p. 454.

oxygen.[1] The iodine value of pure olein is 83·9 (that is, 100 grm. absorb 83·9 grm. iodine), and that of olive oil about 83. Any oil with a higher "iodine value" than olein must contain drying oils, though a lower value does not necessarily indicate their absence if stearin, palmitin, or other saturated fats are also present.

Other Unsaturated Liquid Fatty Acids.—Of these there are several groups, differing in their degree of saturation, and also probably in their structure. Their glycerides, together with olein, and sometimes palmitin, are the constituents of the seed oils, the drying tendency of which depends on their proportion of unsaturated acids, and the particular group to which they belong. The fish oils contain a peculiar group of unsaturated acids, together with olein, and usually stearin and palmitin, like the other animal fats. Linolenic acid, $C_{17}H_{29}CO . OH$, one of the acids of linseed oil, has six hydrogen atoms less than stearic acid, and therefore three double linkings, and will take up six atoms of iodine. Its theoretical iodine value is 274, while linseed oil itself often has an iodine value exceeding 180. The iodine value of cod-liver oil is sometimes nearly as high. Both oils therefore contain other acids less unsaturated than linolenic. Fish oils appear often to contain also fatty acids with four or more double linkings, and giving octobromides on saturation with bromine.

The "spueing" of leather is often due to the absorption of oxygen and consequent resinification of the oils, and therefore all drying oils, however pure, are capable of producing it, though some are more liable to do so than others (*cp.* pp. 469–471).

Linolenic acid, and probably other allied acids, become converted by absorption of oxygen into solid varnish-like substances, which are important to the tanner as furnishing the principal constituents of japans for leather, in which they are now usually accompanied by cellulose derivatives (p. 478). The unsaturated acids of fish oils seldom give hard varnishes, though menhaden oil (p. 447) is sometimes used as paint-oil for outside work.

Most fats are liable to become rancid by exposure to the air, acquiring a disagreeable taste and smell, and an acid reaction from the liberation of the fatty acids. The changes which take place are somewhat complex.

Ricinoleic acid, the fatty acid of castor oil, is of peculiar constitution, being an oleic acid in which one of the hydrogen-atoms is replaced by a "hydroxyl" or OH group. The solubility of

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[1] Oxygen is not often attached in this simple way, but as two $-OH$ groups or in other more complex groupings.

castor oil in alcohol has already been alluded to. It does not dry, and is an excellent oil for lubricating heavy machinery. It is sometimes adulterated with " blown " oils, which are made from non-drying or slightly drying seed oils, like cottonseed or rape, by blowing air through them in a warmed condition. Under this treatment they increase greatly in viscosity and density and in their solubility in alcohol, but do not acquire the other valuable properties of genuine castor oil. It is a curious point that though oils are generally lightened in colour by blowing, their fatty acids, if freed, are very dark, and often heavier than water.

The " foots " or sediments which oils deposit on standing sometimes consist of animal or vegetable fibres, or mucilage combined with water, but often are simply the harder fats, stearin, palmitin, etc., which crystallise from the oil on cooling. In this case they are re-dissolved on warming the oil. Such oils, which like neatsfoot and tallow oils become turbid in cold weather, are styled " tender."

Analysis of Oils and Fats.—Modern methods are almost entirely quantitative, depending on the determination of certain " values," but as fats are complicated mixtures of many glycerides closely allied to each other, it is not usually possible to separate them into their actual constituents, as, in the language of algebra, there are generally more " unknowns " than independent equations, and we have usually to be content with averages. It may reasonably be hoped that with advances in analytical methods this difficulty will ultimately be overcome, but in the meantime much information about the character of an oil can be deduced from the " values." To do this some knowledge of the chemistry of fats is essential.

" *Fatty Acids.*"—This term is sometimes restricted to acids of the saturated or acetic series, but for our purpose it will be more convenient to apply it to all the acids commonly found in fats in combination with glycerin. Most of these acids are monobasic (viz. combine with only 1 eq. of alkali). All consist of a chain of carbon atoms combined with hydrogen, and terminating in the group $O{=}C{-}O{-}H$ (carboxyl), which gives them their acid character. There are a few dibasic acids with two carboxyl groups.

"*Saturated*" *Acids.*—Of these the simplest member is acetic acid, $CH_3CO.OH$, and the highest found in ordinary fats is arachidic, $C_{19}H_{39}CO.OH$, found in earth-nut or arachis oil, but between them is a complete series, mostly increasing by C_2. Usually the carbon chain is straight, but sometimes branched, a side chain taking the place of one of the side atoms of H. This makes no difference in the ultimate composition of the acid, as the substituted H is replaced by the terminal H of the side chain, and hence such acids are isomeric, and usually differ but little in their properties. The most common and important members of the series are palmitic acid, $C_{15}H_{31}CO . OH$, and stearic acid, $C_{17}H_{35}CO . OH$, but some higher members are found in the waxes, and butyric acid, $C_3H_7CO . OH$, is found in small quantity in butter. The general formula of the series is $C_nH_{2n+1}CO . OH$.

"Unsaturated" Acids.—While in the saturated acids each carbon atom is united to each of its two neighbours by a single link, and its remaining two links are combined with and saturated by hydrogen, in the unsaturated acids one or more pairs of carbon atoms are united by a double link, and are therefore each combined with only one atom of hydrogen. This double link is not so strong as the single link of the saturated acids, and when treated with chlorine, bromine, or iodine, or even with hydrogen itself under the conditions of the hydrogenation process (below), one of the linkages is broken, and combines with two atoms of the new element, in the case of hydrogen being actually converted into the corresponding saturated acid. Oxygen can also combine with the broken link, and does so in several ways, thickening the oil by producing gummy or resinous products in the "drying" oils, or even breaking it entirely in presence of moisture, with the formation of an aldehyde and a new acid of lower molecular weight. This is not without importance in the theory of oil-tannages. The number of double linkages varies in the different series of unsaturated fatty acids, rising from one in the oleic series to three in the linolenic acid of linseed oil which forms hexabromides, and even to four in the acids of some of the fish oils.

Hydrogenation.—The most important advance in the technology of fats which has been introduced in recent years is the method of "hydrogenation" discovered by Sabatier. Though hydrogen will not combine with unsaturated fats or fatty acids with the same ease as bromine or iodine, it has been found that under considerable pressure, raised temperature, and in presence of finely divided nickel as a catalyst, the combination does take place, rendering it thus possible to convert any unsaturated fat into a saturated one, or raise it to any degree of saturation required. Thus whale oil can be converted into a solid fat of the stearin type, and at the same time it is so far freed from fishy taste and smell that it can be used as an edible fat, as, for instance, in the manufacture of margarine. A minute portion of nickel becomes dissolved in the fat, but it is so small that it appears to have no injurious effect. The importance of the method for soap and candle manufacture can hardly be overestimated, and for leather manufacture fats as hard as deer tallow or American "oleomargarine" can be produced from any soft animal or vegetable fat, or even from fish oil. The process is therefore being very largely used.

The Acid Value is the number of milligrammes of potassium hydrate required to neutralise the *free* fatty acid in a gramme of the oil or fat. It is determined by titrating the oil in the cold with a N/10 alcoholic solution of potassium hydrate, with phenolphthalein as an indicator, until a faint pink is produced. In this way the free acids are neutralised, but the fats are not saponified.

The acid value varies with the age and rancidity of the fat, and is most important in oils used for lubrication, as the free acids corrode metals. It is also useful in detecting adulteration of tallow with distilled stearine, which consists principally of free stearic acid. The acid value of a genuine tallow may vary from 3·5 to 50, but for lubrication should not much exceed the lower value.

Saponification Value is the number of milligrammes of potassium hydrate required to combine with the *whole* of the fatty acids present in 1 grm. of fat or oil. It is determined by boiling the sample with a known excess of alcoholic potassium hydrate solution and titrating back the excess. It varies with the molecular weight of the acids present, and is therefore a very useful characteristic of different oils, and its average value is given in a succeeding table (p. 436) for the different oils and fats.

As petroleum oils have no saponification value and rosin oils a very low one, low values frequently indicate adulteration with these substances. Their actual quantity is determined by completely saponifying the fat, and then shaking out the soap solution with petroleum ether, which extracts the hydrocarbons, and evaporating the ethereal solution. Waxes, and sperm and "bottlenose" oils (liquid waxes), naturally contain unsaponifiable alcohols, and wool-fat and many fish oils, especially that of shark-liver, contain these in smaller quantities. For their determination a similar method is used, but ordinary ethyl ether must be substituted for petroleum ether, as the alcohols are not very soluble in the latter.

The saponification value of course includes any acid value present, and to determine the "ether value," or that of the acids combined as glycerides, the acid value must be deducted.

The Iodine Value is, as has been explained, a measure of the unsaturated double bonds of the fat, and is the weight of iodine absorbed by 100 parts of the fat or oil, and is determined by treating a chloroform solution of the substance with a known excess of the iodising mixture, and titrating back with thiosulphate in presence of potassium iodide and starch. Several different iodising solutions are in use which give nearly, but not quite, identical values, that of Hanûs, which is a solution of iodine and bromine in glacial acetic acid, being the simplest, and for our purpose the most convenient. Though both bromine and iodine are absorbed by the oil, the mixture is determined by the analysis in terms of the equivalent quantity of iodine, and is so always stated. Saturated fats, such as pure stearin or palmitin, have *no* iodine value, but in natural hard fats some olein is always present, of which the iodine value is 83·9. This approximates to the iodine value of pure olive oil, which is mainly olein, but contains some palmitin, and probably also traces of some less saturated fat. In drying oils, such as linseed, and in fish oils, the iodine value may rise as high as 190 to 200. The higher the iodine value, the more liable is an oil to "spue" or produce resinous spots if used for currying. This must be distinguished from the tendency to cause a white scum or efflorescence on the leather, which is also called "spueing," but is generally due to the presence of hard fats or free fatty acids. As olein is the only unsaturated fat in a genuine tallow or animal fat its quantity may be calculated from the iodine value, and the higher its proportion the softer is the fat.

Physical characteristics of fats are sometimes useful in judging of purity, and as they are generally rapidly determined, they must not be overlooked.

Specific Gravity (the weight of a cubic centimetre in grammes) is the most important of these, and is easily obtained roughly by the use of a suitable hydrometer, but much more accurately by weighing in a gauged bottle or by a Mohr's balance. As oils expand rather rapidly by heat, the observance of an accurate temperature is important. 15° C. is that usually adopted for oils, but for hard fats a higher temperature, such as the boiling point of water, is more convenient. If a bottle gauged for water at 15° is used, the comparison will be with water at this temperature, though strictly an allowance should be made for the expansion by heat of the bottle itself. The value of specific gravity as a test for oils is much diminished by the fact that it can be adjusted by mixtures of low gravity mineral oils and high gravity rosin oils. Castor oil, with a gravity of ·960, is the heaviest of natural oils, and sperm oil, specific gravity ·880, the lightest. All unsaturated oils increase in gravity by oxidation.

Refractive Index is more easily and rapidly obtained than even specific gravity if an Abbe refractometer is available, but this is a somewhat expensive instrument, and is not usually possessed by tanners; and as both specific gravity and refractive index vary in almost parallel proportion, little is to be deduced from the one which is not equally shown by the other. By combining the two, however, and calculating the "refractive constant," which is independent of temperature, more characteristic figures are obtained, and it has been shown that from this the chemical "values" can be approximately calculated, as the refractive constant depends on chemical constitution, and in general terms is raised by unsaturated linkages and lowered by hydroxyls, and is thus highest in linseed and unsaturated fish oils and lowest in castor and "blown" oils, though both types are of high gravity. A pretty full discussion of the refractive constant will be found in a paper by the present author in the *Journ. Soc. Chem. Ind.*, 17, 1890, p. 1021.

Melting and Solidifying Points.—These are often of importance, especially in currying greases. The melting point is usually slightly higher than that of resolidification. Many fats become thickened and pasty at temperatures much higher than that of complete solidification, and in such cases the solidification point is indefinite. The melting point of mixed fats is always slightly lower than the average of that of the constituents taken separately. The melting point of tallows depends in the proportion of olein to stearin and palmitin.

Oils pressed from animal fats usually contain dissolved stearin and palmitin, which separates and crystallises out at low temperatures. Such oils are called "tender," and if used for fat-liquoring are very apt to cause a white scum of hard fats on the finished leather. Oils for this purpose should be filtered when artificially cooled to a low temperature, and should bear being cooled to freezing point without becoming turbid.

The melting point of the free fatty acids is usually much higher than that of the fats from which they are derived.

The following table of constants gives the average values for the more common oils and fats, but there is some variation in different samples believed to be genuine:—

APPROXIMATE CONSTANTS OF OILS AND FATS

Name of Oil.	Sp. Gr. at 15° C.	Refractive Index, 15°.	Saponification Value.	Iodine Value.	Solidification Temperature. °
Blown Rape	·967	1·481	200	63	
Castor	·965	1·480	180	84	−18
Raw Linseed	·935	1·484	193	175	−16 to −20
Cod-liver (med.)	·926	1·485	185	146	0 ,, −10
,, (Möller's)	·928	1·481	..	165	
,, (brown)	·928	1·482	185		
Coast Cod (mixed)	·930	1·482	185	172	
Whale	·931	1·476	193	118	−2
Sardine (Japanese)	·925	1·479	192	121	20
Seal (pale)	·925	1·478	189	138	−2 to −3
Shark-liver (Scymnus)	·917	1·478	188	102	−16
Mixed Fish	·929	1·480	184	140	
Cottonseed	·925	1·475	193	108	−12
Arachis (earth-nut)	·922	1·474	192	95	− 1
Maize	·922	1·477	190	118	−10
Sesame (Gingeli)	·921	1·475	190	108	− 5
Olive	·916	1·470	193	86	− 2
Rape (Colza)	·915	1·474	176	98	− 2
Neatsfoot	·915	1·474	193	70	Tender
Lard	·912	1·472	193	79	−8 to +6
Sheep-skin grease oil	·917	1·468	197	60	Tender
Egg-yolk oil, hen	·914	1·471	184–190	68–81	+20
Sperm and Bottlenose	·880	1·468	123–135	67–81	Dyson's spermaceti
Mineral leather oils	·85–·92	1·47–51	Nil	up to 20	
Rosin oils	·96–·99 at 60°	1·50–54 at 60°	Resin acids	43–48	
Mutton tallow	·895	1·442	195	40	44 to 45
Beef tallow	·901	1·442	196	42	36 ,, 38
Bone fat	·894	1·451	191	51	15 ,, 17
Distilled stearine	·865	1·445	Variable	..	45 ,, 53
Paraffin wax	·776	1·434	Nil	4	40 ,, 55

NON-DRYING FATS AND OILS

Tallow (Fr. *Suif*; Ger. *Talg*) is the fat of various mammalia, principally of the ox and sheep, but occasionally also of the goat. The mixed fat obtained from all parts of the carcass is known as "rendered tallow," while that obtained from the region of the kidneys (suet) is harder. A substance commonly referred to as " pressed tallow " or " oleo-stearine " is obtained by pressing ordinary tallow, in cloths, in the hydraulic press. The more liquid portion which is expressed is tallow oil, the finer qualities of which are used in making margarine. Oleo-stearine must not be confounded with the " distilled stearine," obtained from Yorkshire grease by distillation and pressure (p. 439), nor with candlemakers' " stearine," which is a mixture of free stearic and palmitic acids.

Pure tallow is white and tasteless, but much of that sold is yellowish and of a disagreeable, slightly rancid flavour. Mutton tallow is usually harder and whiter than that of beef. Goat tallow has a characteristic odour, as have the recovered stearines and other waste greases from glue-works. Buck tallow, which is particularly hard, has now been largely replaced by oleo-stearine.

Beef tallow melts at about 40° C., mutton tallow at 45°.

In chemical composition, tallow consists chiefly of a mixture of the tri-glycerides of palmitic, stearic, and oleic acids, its hardness diminishing with the increase of the last.

Tallow should, when melted, be perfectly clear, turbidity indicating the presence of water or other foreign matters, due either to carelessness in the manufacture or, possibly, adulteration. Traces of phosphate of lime, or fragments of animal tissue, may be present as accidental impurities ; lime, on the other hand, is sometimes added to thicken the tallow and enable it to retain more water ; starch, china clay, whiting, heavy spar, etc., are also occasionally employed. Tallow has been not infrequently adulterated with the distilled fatty acids from wool grease. When this is the case, crystals of cholesterol (see *L.I.L.B.*, p. 181) may be detected by examination of the unsaponifiable matter of the mixture under a microscope. Such adulteration would also give the tallow an unusually high " acid value."

Methods for the proximate analysis of tallow are given in the *Laboratory Book*, pp. 189 *et seq.* nd in the *L.C.P.B.*, ch. xi.

The fats produced by the boiling of fleshings for glue, and by the pressing of sheep-skins, are of the nature of soft tallows. If the fleshings are delimed with acid and boiled fresh the grease is generally of good colour and with little unpleasant odour, but contains traces of free fatty acids derived from the decomposition of the lime-soaps. If the fleshings have been dried and the lime carbonated, the grease will generally be brown, and more or less rancid ; but the lime-soaps are not decomposed, unless the " scutch " or refuse be treated with acid, when a further yield of grease is obtained. Carbonic acid will neutralise lime, but will not decompose lime-soaps. The grease from sheep-skins is generally somewhat brown, and often smells of the volatile acids and other constituents of the tan-liquors, especially if larch bark has been used. These greases are usually much improved in appearance and odour if well washed by boiling or steaming on water, or by blowing a mixture of air and steam through them, or sometimes even by mere heating to a sufficient temperature to evaporate the water and drive off the volatile matters. By allowing the grease to cool slowly, so as to favour crystallisation, till it is of a soupy consistency, and then pumping through a filter press with woollen cloths, the more liquid part is separated easily from a more solid portion, and both may in many cases be used in leather manufacture, the tallow for currying, and the oil in place of neatsfoot oil.

Horse-fat, and especially that from the fatty portions of the neck (Ger. *Kammfett*), as well as various other animal greases, are used in the manufacture of leather. They differ from tallow chiefly in that they have a lower melting point, and contain more olein in proportion to the stearin and palmitin than true tallow, and are consequently somewhat softer. Though often almost white, these greases are sometimes darkened in colour by the products of putrefying animal matter, but this does not, as a rule, interfere with the oil being used for leather dressing. They are usually so cheap that they are but little adulterated; means of determining their purity are, however, given in *L.I.L.B.*, p. 191.

Neatsfoot oil is a yellowish, nearly odourless, oil of bland taste, which is largely employed in the dressing of calf-kid. It has a similar composition to tallow oil and the other oils obtained by subjecting the soft animal fats to great pressure at a low temperature. It is often adulterated with bone oil, lard oil, and cottonseed oil, and occasionally with mineral oil and recovered wool grease.

As neatsfoot oil is somewhat costly, curriers may with advantage often use ordinary animal greases (horse-fat, etc.) after they have had the harder tallow extracted by cooling and pressure, the product thus obtained being, chemically, the same as neatsfoot oil, and in every respect as suitable, while it is much less liable to adulteration.

The true neatsfoot oil is prepared by boiling the feet of cattle, and sometimes of sheep and horses, with water, and skimming off and clarifying the oil which is thus obtained. For use in fat-liquors it should be "racked" or filtered at freezing point.

The physical and chemical characteristics of this oil are described in *L.I.L.B.*, p. 192.

Wool-fat (Fr. *Suint, œsype*; Ger. *Wollschweissfett*) is a grease of high specific gravity, exuded from the sebaceous glands of the sheep, together with organic salts of potassium. It is obtained by extracting wool with solvents; or by washing with alkaline solutions, from which it is recovered by precipitation with acid, and subsequent hot-pressing of the "magma," or, more recently, by evaporating the scouring liquor to small bulk, and centrifuging. Wool-fat is characterised by its low percentage of glycerides, the fatty acids which it contains being mainly combined with higher alcohols (bodies of alcoholic structure, but of a waxlike consistency), and chemically it is rather a wax than a true fat. Among the alcohols which it contains is included a marked percentage of cholesterol and isocholesterol. It is difficultly saponifiable, requiring to be heated to 105° to 110° C. with alcoholic potash under pressure; and even then about 44 per cent. of higher alcohols remain, which are incapable of further saponification. Care must therefore be taken not to assume that unsaponifiable matter in greases which may contain wool-fat is necessarily mineral oil. For details of analysis see *L.I.L.B.*, p. 194.

Pure wool-fat is nearly white, of salve-like consistency and very slight smell, with a density of 0·973 at 15° C. Crude wool-fat is yellow or brown, with an unpleasant and very persistent characteristic smell. Both the pure and the crude wool-fat have an extraordinary power of emulsifying with water, which makes them very valuable as substitutes for dégras in stuffing greases. Lanoline and several other preparations under different names are mixtures of purified wool-fat and water, of which lanoline contains about 22 per cent.

"Yorkshire grease" differs from crude wool-fat in being recovered from the waters employed in scouring woollen cloths as well as wool, and hence contains the free fatty acids of soaps used in scouring, as well as the "oleines," etc., used in oiling the cloth, and although it often contains much wool-fat, it is occasionally destitute of this substance.

Holden Fat consists of ordinary wool grease mixed with fish oil, and is used either as a substitute for or in admixture with dégras (*q.v.*).

Distilled Wool Grease is produced by distilling crude Yorkshire grease with steam. Most of the glycerides are broken up, but many of the free fatty acids, alcohols, and waxes distil over unchanged, though a considerable part is decomposed into volatile hydrocarbons strongly resembling mineral oils. The distillate is separated by cooling and pressure into a liquid "oleine" and a solid "stearine." The latter forms a very valuable stuffing-grease, which in England largely takes the place of the "oleo-stearine" used in the United States, with which, however, it must not be confounded.

Distilled Stearine, prepared as above described, is a pale yellow or brown fat, which varies in hardness and in its melting point according to the conditions of its preparation. It has a characteristic odour which is very persistent, and it consists largely of free stearic and palmitic acids, most of the liquid hydrocarbons formed by distillation being removed with the "oleine."

Olive Oil (Fr. *Huile d'olive*; Ger. *Olivenoel, Baumoel*) finds extensive use in leather dressing, and especially in the manufacture of "fat-liquors" (pp. 378, 471). It is extracted from the fruit of the olive tree by pressure, and of late years from the residues by extraction with volatile fat-solvents. Although it chemically resembles tallow and lard oils very strongly, its adulteration with these substances may usually be detected, at any rate roughly, by the taste and odour of the oil. It is principally characterised, from a chemical point of view, by containing the glyceride of palmitic but not that of stearic acid, and by having a much larger proportion of olein to solid glycerides than most of the non-drying animal oils. At low temperatures olive oil solidifies to a product which can be separated by pressure into a solid tallow-like fat, and a fluid oil consisting essentially of tri-olein.

Olive oil is the type of a non-drying vegetable oil, but though it does not thicken materially on exposure, it becomes rancid somewhat rapidly, and is thus rendered unsuitable for lubrication, the free acids attacking brass and copper. Unless the acidity is excessive it does not appear to injure the oil for leather manufacture, and for some purposes is actually an advantage as aiding emulsification. Free acids in oils may be removed by shaking with sodium carbonate solution.

Olive oil always contains some free acid; which is of importance in the preparation of fat-liquors, as it facilitates the production of an emulsion. This quality may be increased by the addition, when necessary, of a little oleic acid or of sulphated oils.

Olive oil is frequently adulterated with other vegetable oils. Probably the most useful criterion is the iodine value, which is raised by the addition of any seed oil except castor. The refractometer also affords useful indications. Cottonseed, sesame, and arachis (earth-nut) oils are the most frequent adulterants of the better qualities, and in many cases may be recognised by special tests.

Castor Oil (Fr. *Huile de ricin*; Ger. *Ricinusoel*) is the oil expressed from the seeds of *Ricinus communis*, and is a transparent, colourless or pale yellowish liquid, having a faint odour and a disagreeable taste. At a low temperature it thickens and deposits slightly, and at −18° C. it solidifies to a pale yellow mass.

Castor oil is distinguished from all other natural fixed oils by its high density (0·960 to 0·964) and viscosity, and by its solubility in alcohol and its insolubility in petroleum ether. Genuine castor oil is completely soluble in an equal volume of absolute alcohol, or in four times its volume of "rectified spirit" at the ordinary temperature. It is practically insoluble in petroleum ether, but can dissolve an equal measure of that liquid.

For the purpose of the leather manufacturer, the ordinary hot-pressed oil, such as is used for lubricating machinery, is quite as good as the more costly cold-pressed oil which is used for medicinal purposes. It is generally imported in tins holding about 40 lb. of oil. Castor oil, and castor-oil soap made as described on p. 427, are very good for fat-liquors, seeming to interfere with dyeing and glazing less than most other oils. Boots oiled with castor oil may be blacked at once, and will take a good polish.

The only oils which are usually mixed with castor oil are "blown" or oxidised seed oils, or resin oil. Any other oils would so seriously lower the specific gravity as to render their use impracticable. For the detection and estimation of these the *Laboratory Book* should be consulted, or if fuller details are required the reader is referred to Lewkowitsch's *Oils, Fats, and Waxes*, or to Allen's *Commercial Organic Analysis*, vol. ii.

Sulphonated (perhaps more properly "sulphated") castor oil or Turkey-red oil is now largely used for "fat-liquoring," for which it was probably first employed by the author about 1890. This material—which must be carefully distinguished from the olive oil preparation which is also used for dyeing cotton a Turkey-red colour—is made by treating castor oil with one-quarter of its weight of strong sulphuric acid (specific gravity 1·8), adding the latter in very small quantities at a time, and taking care that the temperature of the mixture at no time exceeds 35° C. The mixture is then allowed to stand for twenty-four hours, with occasional stirring, and is washed with its own volume of water, allowed to stand until the water has all separated, and the oil is then syphoned off. If desired, the oil may be further washed once or twice with a solution of strong brine, but this is of doubtful advantage, and should in no case be excessive. The washed oil is finally neutralised by the cautious addition of about one-hundredth of its volume of strong ammonia solution (sp. gr. 0·880).

If properly prepared, Turkey-red oil (sulphonated castor oil) will, when *largely* diluted with water, bear the addition of ammonia to alkaline reaction without showing any turbidity even on standing several hours. If a turbidity is produced, it indicates that the castor oil used was impure and contained some oil rich in stearin.

The alcohol test described on p. 441 may also be applied, as the oily layer will be entirely soluble if castor oil alone was used in the preparation of the red oil.

Turkey-red oil usually contains about 50 per cent. of fatty acids (Allen).

Linseed Oil (Fr. *Huile de lin* ; Ger. *Leinoel*) is used by leather manufacturers in the preparation of the japan for making "patent leather" (p. 478), and to some extent also in currying, for oiling off levants and moroccos, though for these purposes it has been largely superseded by mineral oils. It is obtained from the seeds of the flax plant, *Linum usitatissimum*, chiefly grown in Russia and India. The Russian seed is usually mixed with that from hemp, which also yields a drying oil, to the extent of about 20 per cent., while that from India, being grown as a mixed crop with mustard and rape, is never perfectly pure. The Baltic oil is considered best for japans, and is improved by storing for a considerable time in tanks in a warm place.

When obtained by cold pressure of the seeds, previously ground and damped, linseed oil is of a bright yellow colour ; if a higher temperature be used in the extraction the oil is more or less brown, and tastes much more acrid. On exposure to air linseed oil turns easily rancid, absorbs oxygen, and if spread out in a sufficiently thin film it dries to a neutral substance (linoxyn), which is insoluble in ether, but pretty soluble in alcohol. This property is the one on which the chief value of linseed and other "drying oils" depends.

Linseed oil is chiefly adulterated with other seed oils, cotton-seed being the most often used for this purpose, though menhaden and various other fish oils are occasionally employed. As the density of raw linseed oil varies between 0·932 and 0·936 at 15° C., the addition of other seed oils or of mineral oil would cause an appreciable lowering of this figure, whilst rosin or rosin oil would raise it. A judicious admixture of both mineral and rosin oils would give a product of normal density, but would much lower its iodine value. Fish oils can be detected by their characteristic smell, especially on warming.

Various methods have been proposed for judging the quality of linseed oil, but none of them are perfectly satisfactory. The best oil is that which dries the most perfectly; but the rapidity of the drying, and the consistency of the dried product, are most important factors which must also be taken into account. The iodine value, which is a measure of the drying power, should not fall much below 180.

A satisfactory practical test, recommended by Allen,[1] consists in mixing the oil with three times its weight of genuine white lead, and covering a perfectly clean glass surface with the paint. An exactly similar experiment is made simultaneously with a standard sample of linseed oil, and the rates of drying and the characters of the coating of paint compared.

J. Muter has simplified this test by merely flooding a plate of glass with the oil and then exposing it to a temperature of 38° C. (100° F.) in a good current of air. The time required for drying, to such an extent that the coating will not come off when lightly touched, is noted, and compared with standard samples of oil. By applying the finger at intervals to different parts of the film surface the progress of the drying can be readily observed.[2]

Boiled Oils.—The capacity of linseed oil for thus drying is much enhanced by heating, with addition of "driers," to a temperature of 130° C. and upwards, while passing a current of air through the oil and then increasing the temperature until the oil begins to effervesce ("boil"). Large quantities of linseed oil are now treated in this way for use in the arts. The driers used are metallic salts, principally those of lead and manganese, which apparently act as oxygen-carriers. Litharge was formerly most commonly used, but its place has been taken to a considerable extent by acetate, borate, and resinate of manganese. From 1 to 2 per cent. of either litharge or manganese borate may be used, though less quantities produce a marked effect. Apparently litharge gives the most rapid drying, and manganese a much paler colour.[3] Linseed oil is usually darkened by boiling, and increases both in actual weight and in specific gravity and viscosity. The chemical reactions which take place in boiling are not well understood, but it is in the main a process of oxidation

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[1] *Commercial Organic Analysis*, ii. p. 122.

[2] Kathreiner stated that this method is a useful test for fish and liver oils, those which dry most rapidly being specially liable to "spue."

[3] *Cp.* F. H. Thorpe, *Abst. Jour. Soc. Chem. Ind.*, 1890, 628, from *Technology*, Quart., iii. pp. 9–16; also p. 479 of this book.

and polymerisation, perhaps accompanied by the formation of anhydrides of the fatty acids, and a portion of the drier remains dissolved in the boiled oil. These driers may be detected by boiling an ounce or so of the oil with dilute hydrochloric acid, allowing the mixture to separate into two layers and then syphoning off the lower into another vessel, and testing for metals (lead, manganese, zinc) or acids (boric, oxalic, etc.).

Black japan for patent leathers is made by boiling linseed oil, without blowing air through it, for at least seven or eight hours with Prussian blue or with oxides of iron. The japan is brownish rather than blue in colour, and it is probable that the Prussian blue serves merely as a source of iron oxide, which acts both as a colouring matter and a drier. Other driers, such as litharge, are sometimes added, and for coloured enamels other pigments are substituted for the Prussian blue. Most japans now contain nitro-cellulose dissolved in suitable solvents (see p. 483).

Cottonseed Oil (Fr. *Huile de coton* ; Ger. *Cottonoel or Baumwollensamenoel*) is now expressed in enormous quantities in the United States, on the continent of Europe, and in Great Britain. The crude oil contains a very characteristic colouring matter which, though naturally ruby-red, is sometimes so intense as to make the oil appear to be nearly black. This colouring matter causes the oil to produce stains, and is therefore removed by a process of refining, and a product of a straw- or golden-yellow colour is thus obtained. The refining is usually effected by shaking the crude oil with a cold 5 per cent. solution of caustic soda, using about ten times as much oil as soda solution.

Cottonseed oil is, on account of its price, seldom or never adulterated, but is itself frequently employed as an adulterant of olive and neatsfoot oils. It is a semi-drying oil, and unsuitable for most purposes in leather manufacture. For a description of its characteristic properties, both chemical and physical, the reader is referred to Lewkowitsch's *Oils, Fats, and Waxes*, or to Allen's *Commerical Organic Analysis*, vol. ii.

Sesame Oil (Fr. *Huile de sésamé* ; Ger. *Sesamoel* ; Teel oil, Gingeli oil) is another seed oil, usually of paler colour than cottonseed oil, but resembling it in having scarcely any odour, and possessing a bland and agreeable, though not very characteristic, taste. It is often used as an adulterant of olive oil.

Sesame oil is a non-drying oil, which does not easily turn rancid. When present in other oils, it may be detected by agitating 10 c.c. of the sample with 5 c.c. of concentrated hydrochloric acid in which 0·1 grm. of white sugar has previously been dissolved. After shaking together for at least ten minutes the oil and acid are allowed to separate, when, if sesame oil be present, the acid layer will have a marked rose colour, the intensity of which increases with the amount of sesame oil in the sample (Baudouin's test).

Sesame oil is largely used in India for oiling tanned sheep- and goat-skins (" Persians "), and has the characteristic property of being assimilable in large quantities by leather without the latter appearing oily. East India tanned skins often contain 25 and even 30 per cent. The oil is applied to them in the wet condition before they are dried. It is easily detected in the oils extracted from these skins by Baudouin's test. The oil seems well adapted for many purposes in leather manufacture.

Cod Oil (Fr. *Huile de morue*; Ger. *Leberthran*) is by far the most important oil used by leather manufacturers, and is obtained from the liver of the common cod-fish (*Gadus Morrhua*) and several other members of the genus *Gadus*. The chief seats of the cod fishery are the coasts and banks of Newfoundland, Nova Scotia, the Gulf of St Lawrence, the coasts of Norway, Denmark, and Germany, the Dogger Bank in the North Sea, and the shores of Alaska in the Pacific Ocean.

The oil was formerly obtained by keeping the livers of the fish in large wooden vats, stirring constantly until so much decomposition had taken place that the cells containing the oil burst, and the oil thus released rose to the surface and was skimmed off with wooden ladles. The crude oil was allowed to deposit any suspended matters by sedimentation in a tank, and was then poured into casks ready for sale. The " brown oil " so often used by tanners was obtained by boiling the solid matter left after extracting the oil as above in iron tanks until all the water had evaporated; the oil thus liberated was then strained off, clarified, and put into barrels.

The purer qualities of cod-liver oil are now obtained by boiling the livers with water and skimming off the oil which rises to the surface. Three grades are on the market at the present time: medicinal, or ordinary bright; an inferior " light brown "; and " dark-brown," or " tanners' oil." It is probable that these steam-extracted oils are much more liable to " spue " than those extracted by the old method at a higher temperature, since Eitner[1] has shown that seal oils extracted at a low temperature spue badly, but lose the tendency if heated for some time to 250° to 300° C.

Genuine cod oil, as suitable for use in leather manufacture, is

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[1] *Gerber*, 1880, p. 244.

always more or less brown in colour, of specific gravity about 0·928, and refractive index 1·482. At present prices it can only be adulterated with other fish oils, rosin, or mineral oil, or with water, gelatine, or mucilage. Of these, rosin oil and petroleum are the most frequently employed in sophistication.

An inferior variety of oil, known as "coast cod," made from the livers of various fish, such as ling, haddock, and hake, is also sold, but, as it is frequently mixed with oils from other fish refuse, it has a very poor reputation.

Cod oil, together with most of the other oils obtained from fish livers, has the property of producing an intense reddish-violet colour when a drop of strong sulphuric acid is dropped upon ten or fifteen drops of the oil contained in a white porcelain tray or saucer. The reaction succeeds still better if, instead of the oil itself, its solution in chloroform, carbon disulphide or tetrachloride is employed. This test, although very useful for the detection of liver oils when they are present in oils of a totally different character, such as rape or olive oils, does not in any way indicate whether a sample of fish oil is pure or otherwise. A very similar reaction is given by cholesterol which is present in wool-fat.

Shark-liver Oil (Fr. *Huile de requin*; Ger. *Haifischthran*) is obtained from the liver of the "basking shark," or "ice-shark," chiefly caught off the coast of Norway; but the livers of the dog-fish, which is a miniature shark, and several allied fish also are sometimes substituted.

Shark oil has been employed in tanneries as a substitute for cod-liver oil, but, according to Lewkowitsch and to Allen, it is no longer employed in England. From its pale colour it is probably principally used to improve the appearance of darker oils. According to Eitner,[1] its use causes leather to "spue" badly if not previously heated.

Shark oil is characterised by the very notable proportion of unsaponifiable matter which it contains, which is of the same character as that of sperm oil, and not easily removed from its soap solution by petroleum ether, and where shark or similar oils are suspected, ethyl ether should be used for extraction. It gives a strong violet-blue coloration with concentrated sulphuric acid, the reaction being even more marked than with cod-liver oil itself, and of a bluer violet.

Whale Oil (Fr. *Huile de baleine*; Ger. *Wallfischthran*) is extracted from the blubber of various species of whale, and often contains traces of spermaceti, the substance which characterises

[1] *Gerber*, 1886, p. 266.

the oil from the sperm whale. This yields on saponification higher alcohols, which are found in the unsaponifiable matter; but in ordinary whale oil the total unsaponifiable matter seldom exceeds 1½ to 2 per cent. Whale oil is largely used on the Continent for "chamoising" (*q.v.*), and is consequently a constituent of dégras. It is much less oxidisable than cod, and is now often hydrogenated to a consistent and tasteless fat.

Seal Oil (Fr. *Huile de phoque*; Ger. *Robbenthran*) is obtained from the common rough-coated seal, abundant in the Arctic regions. It bears a strong resemblance to both whale and fish oils, and cannot be detected in mixtures of these. The Swedish "Dreikronenthran" (Three Crown Oil) is a mixture of seal and fish oils. As genuine seal oil only contains about ½ per cent. of unsaponifiable matter, its adulteration by mineral or rosin oils may be detected by a determination of the matter extracted by petroleum ether after saponification of the oil (see *L.I.L.B.*, p. 178). It is a curious, and not wholly explained, fact that while seal oil extracted from the fresh blubber is a pale yellow, that from the blubber adhering to seal-skins is a very dark brown or almost black.

There is no simple test by which the purity or otherwise of a sample of oil can be determined, as the dealers know all the best tests which the users could try, and fake up their oils accordingly. For instance, if petroleum is to be added surreptitiously to a cod oil, the decrease in specific gravity of the oil caused by this addition would be corrected by the addition of a suitable quantity of soap or rosin oil, which would scarcely affect the colour, taste, or odour of the sample. The only satisfactory method of detecting adulteration is to submit the oil to a complete chemical examination, and for this purpose *L.I.L.B.*, pp. 156 *et seq.*, *L.C.P.B.*, ch. xi., or the larger text-books already named may be suitably consulted.

Menhaden Oil (Porgie oil, Straits oil) is largely used in certain districts as an adulterant or substitute for cod oil. It is obtained from the *Alosa Brevoordia* or *menhaden*, a member of the herring family, about a foot long. The fish is caught on the Atlantic coast of America, and is so plentiful that it is very doubtful whether cod oil can ever compete with it successfully in price. The fish are boiled in steam kettles, the oil squeezed by hydraulic presses, clarified, and bleached by exposing to the sun in shallow glass-covered tanks. An inferior grade is known as "Bank oil." Menhaden oil is chiefly characterised by its very high "specific temperature reaction" (*L.I.L.B.*, p. 169), which is about 306.

Its iodine value is also high. It is not a good leather-oil, being very liable to " spue."

Many other varieties of oil extracted from the bodies, and not from the livers only, of fishes are classed as *fish oils*. Menhaden oil is the principal of these ; but Japanese oil, sardine and herring oils, and those obtained from the refuse of other fish are scarcely less important, though as they are derived from such different sources it is not possible to quote any definite characteristics by which they may be identified when mixed with more valuable oils. They are usually very liable to " spue."

Fish Tallow, which, according to Eitner, is a good and cheap substitute for dégras, is the solid grease obtained from different kinds of fish oil by subjecting them to a low temperature and separating the matter which is thus precipitated, or (as in China and Japan) the solid fat which is extracted at the same time as the oil from the body of the fish. Formerly fish tallow was only obtained from and with Japanese train oil, but it is now obtained from whale blubber. This latter yields a very pure form of the tallow, which does not need any rectification ; but the Japanese variety, which is obtained from fish of the herring family, contains a sort of fish glue, which greatly deteriorates the quality of the product. By careful purification, however, this glutinous matter may be removed, and the refined product has none of the leather-staining properties so characteristic of the crude tallow. The refined tallow is sold in square flat cakes, melts at 42° C., and is not quite so stiff as ox tallow.

Dégras and *Sod Oil* are products of chamois leather dressing (p. 459) which are used in currying. Skins are treated with marine animal oils and submitted to oxidation, and the surplus and partially altered oil is recovered. In the French method whale and seal oils as well as liver oils are used, and the oxidation is slow and gradual, and the residual oil, being liquid, is recovered by pressure, and constitutes *moellon*, of which the first pressing (*première torse*) is the best. This is never sold for currying in its original purity ; but, mixed with further quantities of fish oils, tallows, and sometimes wool-fat, it constitutes the ordinary dégras of commerce. The additions, though they lower the value, are not to be considered as simple adulterations, since the *moellon* alone would be less suitable for the purpose. After removal of as much oil as is possible by dipping in hot water and pressing a further quantity is recovered by washing with solutions of potash or soda, from which it is separated by addition of acid, and constitutes a lower quality of dégras. The *moellon* is of such value as a currying material that factories are run in which chamoising is carried on solely for its production, the skins being oiled and oxidised repeatedly till reduced to rags. It is also manufactured by direct oxidation of marine oils.

In the English method of chamoising liver oils are almost exclusively used, and the oxidation is much more rapid and intense, the skins being packed in boxes or piled and allowed to heat. The product obtained in this way is much more viscous, and can only be recovered by scouring with alkalies; and the product, recovered with acid, constitutes sod oil. In many English factories a modified method is now adopted, and a product recovered by pressure which scarcely differs from *moellon*.

An important peculiarity of dégras and sod oil is its ready emulsification with water, which from its mode of preparation it always naturally contains, and which should be present in a good dégras to the extent of not less than 20 per cent. Such a mixture, containing water, is a sort of natural fat-liquor, and is absorbed much more perfectly by the skins than an oil alone. Sod oils, however, are frequently "evaporated," or deprived of water by heating above 100° C., with the object not only of effecting a fancied improvement, but of getting rid more completely of the sulphuric acid which the water is apt to contain. This makes them more homogeneous, and consequently much darker in colour. It is not easy to neutralise the acid in an aqueous sod oil by direct addition of alkali; possibly ammonia is best adapted for the purpose; or a suggestion, I think due to Eitner, may be adopted, of incorporating a small quantity of a suitable soap. In any case, very complete mixture is required. If the sulphuric acid used in recovery has been insufficient for complete neutralisation of the alkali, the sod oil will naturally contain soaps, and sometimes also free alkali. Free acid and free alkali are both injurious to leather, the former if anything the more so, darkening the colour, and even rendering the leather tender. When dégras is used in mixture with other fats, care should be taken not to raise the temperature of the mixture so high as to drive off the water, to which a good deal of its special efficacy is due.

The chemical changes which take place during the chamoising process are as yet incompletely understood. A large proportion of the glycerin is dehydrated during the "heating," forming acrolein (acrylic aldehyde), to the action of which it is very possible that the actual conversion of the skin into leather is due,[1] while the fatty acids also undergo oxidation. Dégras

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[1] This is negatived by the discovery of Mr J. T. Wood that good chamoising can be done by the free fatty acids alone, but the residue is not a satisfactory dégras (see p. 461).

therefore always contains considerable quantities of oxidised fatty acids, which are sometimes associated with nitrogenous products from the skins, and which are soluble in alcohol, but insoluble in petroleum ether. To these products Simand gave the name of *Degrasbildner* (dégras-former, Fr. *dégragène*), and it has been considered a measure of the quality of the dégras, but its exact value and function is rather doubtful. According to Simand, a genuine dégras should contain not less than 15 to 20 per cent. of the dégras-former as estimated by his method, calculated on the dry oil, and a smaller percentage is also present in the original fish oils. (For method of estimation see *L.I.L.B.*, p. 182.) It is now known to be simply an oxidised oil product, and only accidentally contains nitrogen.

As the process of dégras manufacture is obviously mainly one of oxidation, many attempts have been made to produce it by direct oxidation of fish oils without the agency of skins, both by blowing air through the oil, and by addition of oxidising agents such as nitric acid. Eitner states that such oxidised oils are more liable to " spue " than the original oils, as they already contain large quantities of resinised products ; but this is certainly not true of all artificial dégras, some of which answers its purpose perfectly as a currying material, though it is very probably justified in other cases. Of course the methods of successful manufacturers are kept as profound secrets.

Dégras and sod oil, when deprived of water, are dark and viscous oils, of high specific gravity (0·945 to 0·955), and therefore heavier than the oils which have been employed in their manufacture.

Waxes, as has already been stated, differ in their chemical character from true fats, in that their fatty acids, which are mostly of high molecular weight, are combined, not with glycerine but with alcohols, also of high molecular weight and of wax-like consistency. Most waxes are solid bodies of high melting point, but some oils, especially sperm and bottlenose oils, are chemically liquid waxes ; wool-fat contains a considerable proportion of waxes ; and many marine oils, such, for instance, as shark-liver oil (p. 446), contain waxes in smaller quantity in mixture with true fatty oils.

Sperm Oil (Fr. *Huile de cachalot* ; Ger. *Spermacetioel, Walratoel*) is obtained from the sperm whale, an inhabitant of the Antarctic seas. " Arctic sperm " (Ger. *Doeglingthran*) is a very similar oil obtained from the " Bottlenose whale." These oils are very fluid, do not dry, and are excellent lubricating oils for light machinery, and also good lamp oils. They contain little if any glycerides, and about 40 per cent. of unsaponifiable solid alcohols, which are soluble in ethyl alcohol, and must not be confused with ordinary unsaponifiable mineral oils, which are frequently used as adulterants in mixture with fatty oils to adjust gravity and the "saponification value." Mineral oils are liquid, and insoluble in alcohol. Sperm oil is the lightest of ordinary oils, its gravity being only about 0·880 at 15° C. From its price it is particularly liable to sophistication. It is used in leather manufacture in the finishing of some fine leathers, and sometimes as a constituent of fat-liquors. Spermaceti, a wax also obtained from the sperm whale, is an occasional constituent of leather polishes.

Bees'-wax (Fr. *Cire des abeilles*; Ger. *Bienenwachs*) is one of the most important waxes for the leather dresser. As is well known, it is obtained from the honeycomb of the ordinary bee. It is a yellowish solid body, fairly plastic when fresh, and of "waxy" feel. At low temperatures it is brittle and of fine granular texture, and when pure is almost tasteless. It is often bleached by repeated melting and exposure to sunlight. As wax always contains a considerable amount of pollen, it may be identified when in admixture with other substances by means of the microscope.

Bees'-wax is almost insoluble in cold alcohol, but boiling alcohol dissolves out the contained cerotic acid, which crystallises from it on cooling. The wax is saponified by alcoholic potash, but the resulting myricyl alcohol (about 54 per cent.) is not capable of further saponification.

Bees'-wax is frequently adulterated. Water and mineral matters (ochre, gypsum, etc.), also flour, starch, tallow, stearic acid, japan wax, carnaüba wax, rosin and paraffin wax, are among the substances most commonly used in its sophistication.

The detection of these, and especially of the other waxes, is so difficult that it will not be described here. The reader is, however, referred to Lewkowitsch's *Oils, Fats, and Waxes* for further information.

Carnaüba Wax (Fr. *Cire de carnauba*; Ger. *Cearenwachs, Carnaubawachs*) has come largely into use owing to the advent of the coloured leather shoe. As it is a very hard wax, melting at 83° C., it has become very popular with boot-polish makers, its low price being also in its favour. Carnaüba wax is an exudation from the leaves of *Copernica cerifera*, a palm indigenous to Brazil, and is, on this account, often known as Brazilian wax. It is difficult to saponify, and with different experimenters has yielded very varied results on analysis; it is generally agreed, however, that it is a complicated mixture of several of the higher alcohols and acids.

Japan Wax is not a true wax, but a fat consisting mainly of the glycerides of palmitic acid, and completely saponifiable. It is a pale yellow, hard, waxy substance obtained from the berries of a sumach (*Rhus succedanea*, etc.). At ordinary temperatures its specific gravity is exactly that of water, and it melts at 56° C. Any admixture with other fats would lower the melting point, but japan wax is often adulterated with 15 to 30 per cent. of water. It is chiefly valuable to leather dressers as a substitute for bees'-wax on account of its lower price.

Volatile or Essential Oils

These oils are distinguished from those described in the previous section in that they are capable of distillation without undergoing any serious amount of decomposition, and are chemically of quite different constitution. They occur to some considerable extent in Nature, but those of most importance to the leather trade are produced by the decomposition of more complicated materials. They all have characteristic odours, and often considerable antiseptic power.

Birch Oil is by far the most important of this class of oils so far as the leather dresser is concerned, since it is the substance which gives to " Russian leather " its characteristic odour.

The oil is obtained by destructive distillation from the white outer bark of the birch *Betula alba*, and the process by which the peasants conduct this is one of the rudest that can be imagined. A cauldron is filled with dry birch-bark, closed, and heated over a fire. The vapours which are evolved are carried, by means of a pipe, to another vessel which is buried in the ground, and are there condensed. The dark-brown liquid (birch tar) is allowed to cool, and the tar which rises to the surface skimmed off. The tar is sometimes distilled, and an oil is thus obtained which does not give the true birch-oil scent very strongly, though occasionally sold as a refined oil. The true odorous substance is evidently of very high boiling point, and remains mainly in the tar.

The birch tar is almost entirely used for giving leathers a " Russian " odour, for although it smells somewhat strongly of tarry products, the oils causing this smell are far more volatile than the birch scent itself, and therefore disappear on storing the leather a short time. Tar obtained from various species of pine is sometimes substituted for birch tar, but it may readily be distinguished from the latter by the odour and the difference in the specific gravity. Birch tar has a specific gravity of 0·925 to 0·945, whilst fir tar has one of 1·02 to 1·05; thus the former floats on water, while the latter sinks if it be entirely free from enclosed air. Fir tar, too, gives up a yellow colouring matter to water shaken up with it, while birch tar leaves the water colourless. Birch tar has a distinctly acid reaction, and must not be kept in iron vessels (see p. 287).

The leaves and twigs of American black birch (*Betula lenta*) when distilled with water or steam yield an oil which is practically identical with that of *Gaultheria procumbens* (wintergreen), and consists almost entirely of methyl salicylate.[1] It is clarified, and to some extent decolorised, by filtration through woollen blankets and redistillation. A ton of brushwood is said to yield about four pounds of oil. This oil has quite a different odour to that of the real Russian oil, and cannot be used in the scenting of "Russia" leather. Sandalwood oil with a little black birch or wintergreen oil is sometimes employed for scenting small fancy articles, and bears considerable resemblance to the true "Russia" leather odour. Black birch, aniseed, sassafras, and various other essential oils are occasionally used in small quantities as preservatives, and to cover disagreeable odour in blood-seasonings, cements, and other products used in the leather trade. The methods employed for their detection and estimation do not, however, come within the scope of a work such as the present one. Most essential oils have considerable power as antiseptics, and in preventing mildew and the attacks of insects.

MINERAL OILS AND WAXES

This class of bodies is totally different in chemical constitution from the true oils and waxes, containing neither glycerides, fatty acids, nor alcohols, but consisting of carbon and hydrogen only, approximately in the proportion of one atom of the former to two of the latter. They occur in underground lakes, from which they are obtained by springs or borings; or in shales, from which they are separated by distillation. It is commonly supposed that they have been formed, at some remote period of the earth's history, by the decomposition of animal and vegetable matters at a high temperature and under great pressure[2] (*cp.* p. 428).

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[1] Methyl salicylate is now made synthetically. It has a pleasant odour, somewhat different from that of the natural product.

[2] Oils from wells or springs are technically called "petroleum oils," those from shale "paraffin" oils, but, chemically, there is no definite distinction.

The mineral oils and waxes are largely capable of being distilled without decomposition, but if heated to high temperatures are readily " cracked " or broken up into simpler and generally more volatile compounds—a fact which is employed in the production of gas, and the utilisation of some of the heavier products for motor spirit.

They differ greatly in their gravity and boiling point, but not much in their ultimate composition, consisting largely of saturated or nearly saturated hydrocarbons (*cp.* p. 429), and hence are little liable to oxidation, and acted on by few chemical reagents. From their constitution they are of course unsaponifiable, and in this way can be separated from fats and oils with which they have been mixed. (For particulars of the method see *L.I.L.B.*, p. 178, and *L.C.P.B.*, ch. xi.) Attempts have been made by oxidation to give them an acid character and fit them for soap-making, and by means of emulsifying agents considerable quantities can be incorporated in soaps.

The heavier mineral oils are a good deal used in mixture with other oils and fats for stuffing leathers, those of a specific gravity of 0·880 to 0·900 being usually most suitable. They are quite incapable of " spueing," and are useful in lessening that tendency in other oils with which they are mixed. They have not, however, the same affinity for the leather fibre as some of the true oils, and are to a certain slight extent volatile, and should generally be used in mixture rather than alone.

Most mineral oils, when held so that a strong light (daylight or electric light rich in ultra-violet rays) falls upon them, show a green or violet fluorescence or " bloom." This is very persistent, even when the oil is mixed with a large volume of other oils, and is often relied upon as a means of detecting them when used as adulterants. The test is, however, not infallible, since the effect is due to impurities which may be removed by purification, or masked by the addition of such substances as nitrobenzene or nitronaphthalene, and it also occurs in the hydrocarbon products produced in the distillation by steam of animal oils, and is occasionally seen to some extent even in oils which have not undergone distillation.

Vaseline and Vaseline Oil are the most viscous and densest of the petroleum oil products. They differ from the solid paraffins in chemical constitution, though their ultimate composition is almost the same, and some of them are ring-compounds (cyclo-paraffins). They are often useful constituents of stuffing greases.

Paraffin Wax consists of a mixture of hydrocarbons similar in chemical constitution to the paraffin and petroleum oils, but of higher boiling point, and solid at ordinary temperatures. Its hydrocarbons are mostly saturated, and hence very stable bodies, and little liable to oxidation. They are completely unsaponifiable, and unaffected by boiling with alcoholic potash, and in most cases by boiling with strong sulphuric acid, by which they may be separated from animal and vegetable waxes or fats with which they have been mixed. They are quite incapable of resinising by oxidation, or of causing " spueing " in leather. They are soluble in petroleum spirit, carbon disulphide, and most of the ordinary solvents of fats, but insoluble in alcohol.

Paraffin wax separates from the liquid oils by crystallisation on cooling, and the remaining liquid which adheres is removed by hydraulic pressing, as in the case of tallow. The hardness and melting point vary according to the extent to which the pressing has been carried and the temperature at which it has been done. The paraffins of higher melting point are as a rule the more costly.

Pure paraffin wax is a white, more or less hard and brittle substance which does not melt so easily as ordinary fats, and is on this account used in stuffing certain kinds of leather, hardening the stuffing grease, and making the leather feel less oily. When melted, paraffin wax forms a thin liquid, more resembling an ordinary petroleum lamp oil than the viscous vaselines and leather oils. On ignition it burns with a bright somewhat smoky flame, and leaves no ash behind. It is found on analysis when mixed with other waxes or oils in the " unsaponifiable matter " (see *L.I.L.B.*, p. 178).

Ozokerit is a natural paraffin material used for the manufacture of ceresin candles, which sometimes occurs in the vicinity of petroleum springs, especially in Galicia. It is of pale yellow colour when pure, and has then a melting point of about 70° C. Its chief impurities are petroleum oils, water, and clay. These are removed by melting the ozokerit, decanting off the clear oil, and filtering it through fine animal charcoal. If liquid oils are present the material is treated with alkali or with strong sulphuric acid, and is pressed before filtering through charcoal. The refined product is termed " ceresin," and is of a more waxy and less crystalline texture than ordinary paraffin wax.

The Rosin Oils are derived from resins, and *mainly* from colophony or common pine rosin, by destructive distillation. Their specific gravity ranges from 0·96 to 0·99, but their chemical composition is very imperfectly understood, and appears to be by no means constant. Like the mineral oils they are " unsaponifiable," but often contain small amounts of soap-forming material (rosin acids).

The detection and estimation of rosin oils is often a matter of considerable difficulty, but further particulars on this point will be found in *L.I.L.B.*, p. 180. From their cheapness they are considerably employed as adulterants of other oils, and their high gravity makes them convenient for adjusting the gravity of mineral oils when used for this purpose, as the latter are usually lighter than the fatty oils. As currying oils they are not particularly suitable, though often employed in stuffing picker bands and other heavily greased leathers. They have considerable antiseptic powers, and for this reason are useful in leather greases, preventing heating and checking mildews.

Rosin itself is occasionally used as an addition to stuffing greases, and is said to increase the waterproofness of the leather, and to give it a drier feel. In mixture with about half its weight of paraffin wax, and with a little grease if necessary to soften the mixture, it is often used in waterproofing mixtures, which can be made to melt at 50° to 60° C. Leather will bear immersion in the melted mixture without scalding if thoroughly dried in a hot stove at a temperature of not less than 50° C. before dipping. Any great increase of the proportion of paraffin wax causes the rosin to separate. Rosin consists mainly of free acids which easily combine with alkalies and alkaline carbonates in boiling. It is hence largely used in the manufacture of soaps on account of its cheapness and to render them more soluble in water. The rosin acids are not so strong as many of the fatty acids, and rosin soaps are therefore somewhat strongly alkaline. Rosin soap, precipitated among the ground paper pulp in the rag engine, by addition of alum or sulphate of alumina, is largely used as a sizing for common papers.

CHAPTER XXVI

OIL TANNAGES, AND THE USE OF OILS AND FATS IN CURRYING

The conversion of skin into leather by the agency of oils and fats is probably one of the most primitive methods, and is used in different ways suited to the skins and fats which are available by savage races in all quarters of the globe. In its simplest form it consists merely in oiling or greasing the wet skin, and kneading and stretching it as it slowly loses moisture and absorbs the fat. Under these conditions the fibres become coated with a greasy layer, which prevents their adherence after they are once separated by the mechanical treatment. At the same time some chemical change takes place in the fibre itself, which has a part in its conversion into leather varying in importance according to the method and fat employed, and of which the chemistry will be best discussed after some slight sketch has been given of the methods themselves.

The finest furs are still dressed by fulling or treading with oxidisable oils, but the most complete sort of oil-leather is that produced by "chamoising" or oil-dressing, a process applied to the ordinary "chamois" or "wash-leathers" (now made from the flesh-split or "lining" of the sheep-skin), and to the manufacture of "buff leather" for military purposes. The process varies somewhat according to the character of the leather, but the manufacture of the common wash-leather may be taken as a type. For this purpose the sheep-splits are freed from the loose and fatty middle layer (p. 62) by "frizing" with a sharp knife on a beam similar to that used for fleshing (fig. 34, p. 195), but much more steeply inclined. The process is rather one of scraping than cutting, and was originally adopted to remove the grain from the deer-skins which were largely used for glove-leathers, since oil-dressing does not easily penetrate a skin with the grain surface intact. The fleshes are usually delimed by drenching, but removal of fat is unimportant. After being well drained they are "stocked" for some time with sawdust till they become partially dry and porous, the common "faller" stocks shown in fig. 26, p. 164, being generally employed. During the stocking care must be taken that the goods are not overheated by the friction produced. When the skins have become opaque from the inclusion of air between the fibres they are, according to the Continental method, shaken out and oiled on the table, and after folding into bundles are put back in the stocks. In England the oil is usually added in small quantities, during the stocking and becomes rapidly and evenly distributed by the motion of the skins. In England cod oil is almost exclusively employed, but on the Continent a considerable proportion of seal and whale oils is used. As the goods are apt to heat, not only from friction, but from the oxidation of the oils employed, they are removed from the stocks at intervals and allowed to cool, usually hung on hooks exposed to the air. In France this exposure to the air is much more considerable than in England, the skins being hung for eight or twelve hours after each stocking. The drying rooms are kept moderately warm, and a good deal of oxidation of the oil takes place in them, which materially affects the character of the product, and especially of the residual oil or dégras, which is afterwards squeezed out of the skins and used for currying (p. 448). Great care is required to prevent any parts of the skins becoming dry before they are completely saturated by the oil, which would cause hard and transparent patches which the oil will not afterwards penetrate. After each exposure to the air the skins are oiled on the table and returned to the stocks. The stocking has to be continued for many hours, even for wash-leather; and as it proceeds the skins lose the smell of limed skin, and acquire a peculiar mustard-like odour from the volatile products of oxidation of the oils. When the skins are completely saturated they are, according to the English method, packed in boxes and allowed to heat spontaneously by oxidation of the oils, during which great care is required, especially at the outset, that the temperature does not rise so high as to destroy the skins. To prevent this they are removed at intervals from the boxes and spread on the floor to cool and then re-packed, and this treatment is continued until the oxidation is complete and the skins cease to heat. During the heating large quantities of volatile and very pungent products are given off, and especially acrolein (acrylic aldehyde, from the dehydration of the glycerin), which is excessively irritating to the eyes. The German method is not unlike the English, but in France the packing in boxes is omitted, and the oxidation is completed in warm stoves, in which the goods are hung on hooks. The heating in this case is much more moderate and the oil less thickened, a result which is partly due to the different oils employed, and which leads to differences in the subsequent treatment of the leather.

In the French process the oily skins are dipped in hot water and wrung[1] or hydraulic pressed, the expressed oil constituting *moellon* or *dégras* (p. 448), and the skins are afterwards washed in a hot soda or potash solution, from which a further portion of an inferior *dégras* is recovered. In the old-fashioned English method the oil became so thickened that it could not be pressed out, and the whole was removed by washing with soda or potash solution, from which it was recovered by the use of acid, constituting " sod oil " (p. 449). Now many English manufacturers adopt a modified method, and remove a good deal of their oil by pressure.

Buff leather, much used for military accoutrements, is made in a similar manner to chamois, from ox or cow hides, the grain of which is frized off with a sharp knife. The bleaching, both of buff and chamois, is done by exposing to the sun in a damp condition, the skins being watered as required with water or fat-liquor, or the alkaline emulsion of *dégras* obtained in washing the skins; or chemically by oxidising agents, such as permanganate of potash or acidified sodium peroxide. If permanganate is used, the leather is treated in a solution of perhaps 5 grm. per litre till of a deep brown colour, and then in a solution of sulphurous or oxalic acid till the colour is removed.

Messrs J. & E. Pullman, of Godalming, made a species of buff leather, which they styled " Kaspine," by treating limed and drenched hides or skins in a drum with a very dilute solution of formaldehyde (" formalin ") rendered alkaline with sodium carbonate (Eng. Pat. 2872, 1898. *Cp.* p. 576). The change to leather took place very rapidly, and the leather was afterwards treated with soap solutions or fat-liquors to feed and soften it. It was almost indistinguishable from genuine buff leather, except that it was white throughout and needed no bleaching. It found considerable application for military purposes. Similar processes are now rather largely used in the production of " washable " glove-leathers, but the details are jealously guarded trade secrets.

A type of leathers which bear a close chemical relation to oil-leathers is that including " Crown," " Helvetia," and fat-tanned leathers. The first leather of the sort was invented by a

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[1] Wringing is done by forming the skins, in pairs of which the ends are turned inside the link, into a sort of chain, one end of which is attached to a fixed hook and the other to a winch, so that the chain can be tightly twisted.

German cabinetmaker named Klemm, by whom the secret was sold to Preller, who manufactured it in Southwark under the name of "Crown" leather. Klemm used flour, ox-brains, butter, milk, and soft fat, which was made into a paste with water, and spread on the limed, drenched, and partially dried skins, which were rolled into bundles, and drummed in slightly warmed drums for some hours; taken out, again dried slightly, and coated with the mixture, and again drummed. For thick hides the process was repeated a third time, drumming in each operation for about eight hours. The leather was used for laces, picker bands, light belts, and other purposes where great toughness and flexibility were required. It was found by further experience (if indeed it was not known to Klemm himself) that the only really essential ingredients of the mixture were the soft fats and flour; and even the latter could, for some sorts of leather, be dispensed with. It was further ascertained that only the gluten or albuminous part of the flour was absorbed by the leather, the starch serving mainly to facilitate the emulsification of the fats. The proportions used in the paste are about seven parts of flour, seven parts of soft fat such as horse grease, two parts of tallow, four parts of water, and a little salt or nitre to act as an antiseptic. Other greases, such as mixtures of tallow and oil, can be substituted for the horse grease, and pipe-clay or ochre may to some extent take the place of the flour, while soap may also be added, and fish oils are occasionally used. The similarity of the mixtures used to the tawing paste in calf- and glove-kid dressing (pp. 247, 252) is obvious, and Klemm had an earlier process in which the operation just described was preceded by a slight alum tannage, and which was almost identical in its detail with the methods now in use for the production of so-called "raw hide." On the other hand it is nearly allied to the production of "Riems," or raw-hide straps in South Africa, for which a long thong is cut spirally from a hide and wound into a sort of skein, which is suspended from a crossbar with a heavy weight at its lower end, and oiled and twisted, with frequent changes of position, until the water is dried out and the thong is saturated with fat, forming a very tough and durable leather. A similar material can be made by fulling or otherwise working grease into a raw hide prepared for tanning. Eitner examined samples of "Crown" leather chemically, by removing the gluten of the flour with an alkaline solution, and found that an imperfectly chamoised leather remained, which, when restuffed with fat, was much less full, and carried a much smaller quantity of grease than before.

Various theories have been proposed to explain the reaction which takes place in the production of oil-leathers. Fahrion has shown that chamoising can be done with vegetable drying oils such as linseed, and the white Japanese leather used for brace tabs is produced with rape oil. Knapp supposed that it was merely a case in which the smallest fibrils of the hide were coated with the products of the oxidation of oils, and so prevented from adhering together, and protected from the action of water by the sort of waterproof coating which was formed. This explanation is scarcely feasible in the face of the fact that chamois leather can be treated even with hot dilute solutions of the caustic alkalies without destruction, while cotton fibres waterproofed by treatment with drying oils have their coating entirely removed by treatment with alkalies. Lietzmann supposed that the whole of the gelatinous fibres were removed in the liming and subsequent treatment, and that the finished leather consisted only of the skeleton of yellow or elastic fibre which exists in the skin, and which is remarkable for its resistance to heat, acids, and alkalies. Unfortunately for the theory, the proportion of these fibres in the entire skin is a very small one, and they exist mainly, if not entirely, in the "grain," which is removed by splitting, their occurrence at all in the flesh-split being doubtful. We know that aldehydes are capable of converting gelatinous substances into a material very similar in its power of resisting hot water and alkaline solutions to the fibre of chamois leather, but the view that acrylic aldehyde, which is derived from the glycerin in the heating of the skins, is the active agent is no longer tenable, since J. T. Wood has shown that excellent chamois leather can be produced by the use of the free fatty acids of fish oils from which the glycerin has been entirely removed. The aldehyde theory is not entirely disproved by this, since aldehydes are produced (see pp. 432, 449) from the splitting of oxidisable oils at the double linkage, and in all cases where perfect chamoising is produced intense oxidation takes place, but it must be admitted that it seems less probable than formerly, and we have still to look for a complete explanation. There is no doubt that the coating of the fibres with oil products does take place, and it is possible that they enter into some sort of combination with the hide-substance which is no longer soluble in alkalies. Such a coating is probably a powerful factor in the leathering of "Crown" leather and other similar products which are not washed out with alkaline solutions. Knapp proved by treating raw pelt, which had been dehydrated with alcohol, with a very dilute alcoholic solution of stearic acid that a thin coating of stearic acid on the fibres would confer great softness and considerable resistance to water. Even where no stearic or other fatty acid is purposely added to alcohol used for dehydrating pelt, traces are present from the decomposition of the natural fat of the skin, and there is little doubt that this is the cause why such alcohol leathers are much more difficult to wet back again to the state of pelt than would *a priori* be expected, and why hide-powder dehydrated in this way is un-

FIG. 103.—Scouring large Seal-skins by Hand.

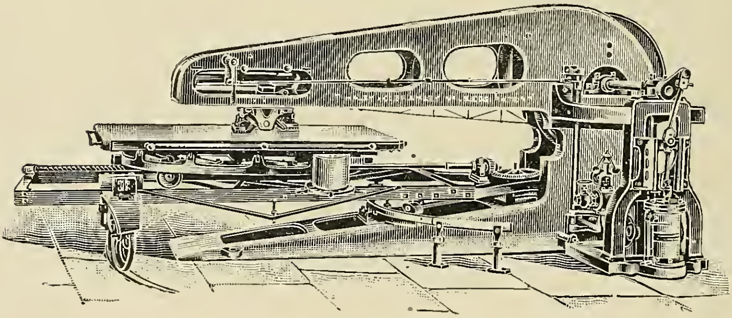

FIG. 104.—Scouring Machine.

suitable for use in tannin estimation from its non-absorption of water.

It is not within the scope of the present volume to describe in detail the processes used in currying, many of which are purely mechanical and of no theoretical interest, whatever their practical importance. The leather is usually scoured with stone, brush, and sleeker to stretch it and free it from "bloom" and loose tan (fig. 103); or by machines such as fig. 104; and is often reduced in thickness by shaving by hand (fig. 105) or by machine (fig. 106). In place of shaving, hides and skins are frequently split into two or more thicknesses. This is done by various machines, of which the "band-knife" shown in fig. 107 is the most important, the cutting tool being a thin steel belt stretched like a band-saw, and sharpened on one edge by an emery-wheel. The use of machines is rapidly superseding hand labour, not only from its lesser cost, but often from its more satisfactory quality.

FIG. 105.—Hand Shaving.

Something must, however, be said about the function of the oils and fats used in currying and their general method of application. It is obvious that the possibility of coating the finest fibrils of leather with a fatty layer is not restricted to raw hide, but is present, sometimes even in a higher degree, in tanned or tawed leathers, in which the fibres are already so far isolated as to make the access of the fat easy. Even the possibility of oil-tannage is not excluded where the fibre is not already completely saturated with other tanning agents, or where these agents, from their nature, have not so firm a hold on the fibre as to be incapable of being displaced by the action of oil-products. It is therefore obvious that we may apply some of the ideas which we have formed with regard to oil-tannages to the action of fats upon tanned leather. In the first place, it must be remembered that gelatinous matters are as a rule insoluble in fats ; and *vice*

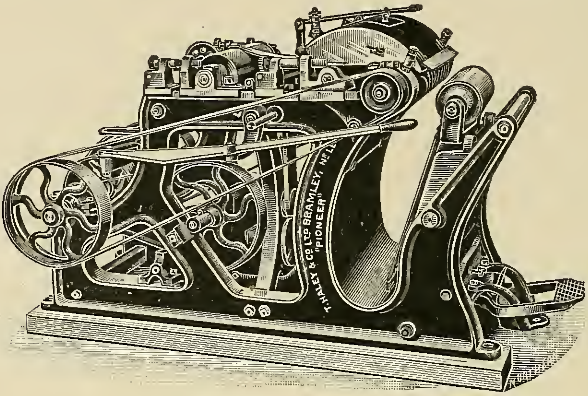

Fig. 106.—Shaving Machine.

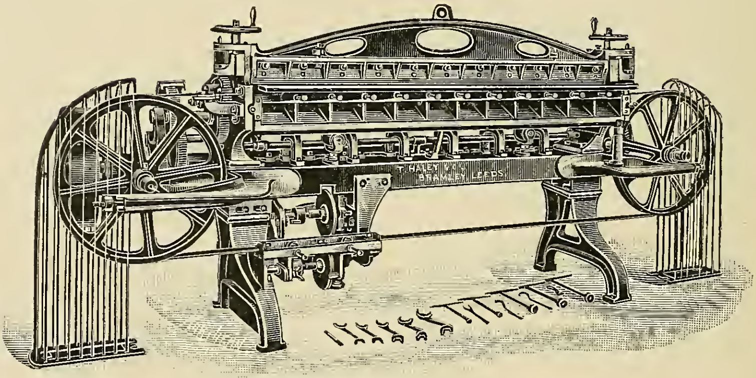

Fig. 107.—Band-knife Splitting Machine.

versa, that fats are incapable of penetrating dry and solid gelatinous fibres. If the skin becomes dry in the chamoising process that part remains raw. It may therefore be concluded that fats and oils have little power in themselves of isolating the fibrils, and that this must be accomplished by other agencies, since if they are still adhering together the fats cannot penetrate them. Hence the necessity of moisture, which keeps the fibres soft and divisible; and with raw hide, the importance of powerful mechanical treatment, which will work the minute globules of fat between the fibrils. In the case of tanned leathers the last condition is less important, since the fibres are already isolated by the tannage, and capillarity assists the penetration. Even in this case the distribution of the fat is much assisted if it is already in a state of fine division (emulsification), and if the surface tension (p. 88) between it and water is low, as is the case with dégras and other partially oxidised oils. On this rather than on any special chemical affinity probably depends the importance of the "dégras-former" and other products of oxidation which are present in dégras, and the difference in penetrating power of different oils. So long as oil remains in an undivided condition so long can it be squeezed out, and the leather will feel and appear greasy; while, when it is thoroughly emulsified and adherent to the fibre, it can no longer be expelled by mechanical means. No doubt the different power of different tannages to "carry grease" without appearing greasy is also related to the degree of isolation of the fibrils and their surface tension with regard to fats. We may judge that the more readily an oil can be emulsified, the more freely and completely it is likely to fix itself on the leather fibre. For this reason, and for their power of emulsifying other oils, the sulphonated fish oils now so largely used on sole leather would probably be useful constituents of stuffing greases.

It is a practically invariable rule that the leather fibre must be wet when it is stuffed. The surface tension (see p. 88) between the water and the fats is less than that of either with regard to air (p. 90); and therefore, as the water dries out of the small interstices of the leather, the fat follows it in, and gradually takes its place. Generally speaking, the amount of water should be such that some exudes in minute drops when the leather is pinched, that is, that not only the minutest spaces between the fibrils are filled, but to a considerable extent even the larger ones between the fibre bundles.

In "*hand-stuffing*" the leather is now coated on the flesh side, or occasionally on both sides, with "dubbing," which is a pasty mixture of fats usually mainly composed of cod oil and tallow, which is applied rather thickly with a brush and smoothed down with the fleshy part of the forearm. When such constituents are melted together the harder fats dissolve in the oils, and as the mixture cools much of the hard fats again crystallises out. To make a good dubbing the cooling fats must be stirred continuously till cool, as otherwise the mixture separates into little globular masses of crystals with liquid oil between them, instead of forming a uniform body of salve-like consistency. The proportions of the hard and soft constituents of the dubbing should be adjusted to the season and to the temperature at which the drying of the stuffed leather is to take place, so that, on the one hand, the dubbing will not melt and run off, and, on the other, that it should not solidify more than is necessary, as only the liquid solution which remains entangled among the crystals can be absorbed by the leather. The solid crystalline fats remain on the surface, and are scraped off by the sleeker in finishing as "table-grease," which is generally re-melted and used over again. It does not answer in hand-stuffing to carry this re-use too far, as the table-grease contains only the harder parts of the fat, with a continually increasing proportion of stearic acid, so that if a dubbing be made continuously of table-grease and oil, in the end little but the latter will be absorbed by the leather, while where fresh tallow is used, a portion of its softer constituents remains dissolved in the oil. The principal function of the harder fats is the mechanical one of retaining the oil on the surface of the leather; and to a certain extent they may be replaced by other solids, such as steatite ("French chalk"), or perhaps other pulpy materials. The use of a portion of soft fat, such as bone-fat, or the better sorts of glue-grease, is quite practicable, especially if mixed with the harder table-grease.

The drying of hand-stuffed leather should be slow, to allow time for the absorption of the grease; and the temperature should be so regulated as to keep the dubbing in a soft but not liquid condition. In winter, if the temperature of the outer air be raised sufficiently for this, the drying will be too keen (*cp.* p. 518), and the water will be dried out before the grease is properly absorbed. It is therefore best, in cold weather, to maintain the ventilation mainly by circulating the air in the room, with little admission from the outside, and in extreme cases even artificial damping of the air may be advantageous. Sometimes the tendency to mildew during slow and warm drying is very troublesome. This may be prevented by the addition of antiseptics to the stuffing grease. Carbolic acid and creosote are effective, but sometimes objectionable from their smell; rosin oil has considerable antiseptic power, and mineral oils also in a less degree. Probably *a*-naphthol would prove an efficient remedy, as it has little odour, and its antiseptic properties are very strong, but it has not been tried by the writer (*cp*. Chapter V.).

In *drum-stuffing* the conditions differ materially from those of hand-stuffing. The goods, in a damp condition, are placed in a drum (fig. 108), which has been heated by steam to as high a temperature as the leather will safely stand. Cold, damp leather may be stuffed in a drum heated to 60° C., and the grease may be run in at the same temperature. The grease should generally be melted and mixed at a somewhat higher temperature. Sometimes steam is merely blown into the drum before introducing the leather to heat it to the required temperature, sometimes a steam coil is placed in the drum itself. A more modern method, which is now largely used in the United States, is to heat by hot air, which is circulated by a fan over an external steam heater and through the drum. The drum is set in rotation, and the stuffing grease in a melted condition is run in through the hollow axle, or, if this is not provided, it is introduced through the door, and the rotation is maintained for twenty to thirty minutes. During the last few minutes the door is frequently replaced by an open grating, or cold air is drawn through the drum by means of the fan, in order to cool the goods, which are

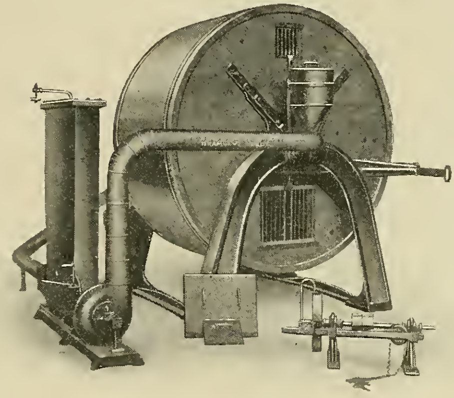
FIG. 108.—Turner's Hot-Air Drum.

set out with the sleeker on the table while yet warm, and dried under much the same conditions as have been described with regard to hand-stuffed goods.

In drum-stuffing the hardness of the grease is limited by its melting point, which must not be so high as to damage the leather, but it may be as soft as is desired. As the grease is forced by mechanical means into the interior of the leather there is no danger of its running off, but the drying must take place at such a temperature as to keep it at least in a partially soft condition, as the drumming only forces it into the coarser spaces of the leather, and does not complete its distribution on the fibre. By the use of exceedingly hard greases, such as "stearine" (p. 440) and oleo-stearine (p. 437), sometimes with additions of paraffin wax, it is possible to introduce immense quantities of grease, and yet to obtain a leather which will board up to a good colour. In America it is not unusual to reckon 100 or even 115 lb. of greases to 100 lb. of leather weighed dry after scouring, or estimated from its wet weight; and the whole of this is absorbed, scarcely anything coming off in "setting." The leather as it comes from the drum is dark brown, but when bent sharply in "boarding" to form the grain, after cooling and drying, the very hard and crystalline fats crumble into white powder, and the leather takes a light and pretty colour. Such leather would of course darken at once if it were held to the fire, but would again brighten on cooling and breaking up with the "board." Some portion of liquid fats, such as dégras or fish oil, should be contained in the stuffing grease, as the solid fats alone will not penetrate to the heart of the fibres, but will leave the leather dry and harsh.

By drum-stuffing it is possible to incorporate solid matter with the leather, and barytes (ground heavy-spar or barium sulphate) was formerly much used for this purpose, but has now been abandoned as too easily detected. Organic fillers, such as flour, casein, rosin or rosin soaps, might probably be used in some cases with advantage; and most colloidal precipitates would be absorbed. Glue is often used as a stiffener in rolling splits for insoles. Glucose is still used as an adulterant of leather, but is not introduced in the drum, but by painting the goods with syrup before stuffing. It not only adds weight, and gives the leather a lighter colour than an equivalent quantity of grease, but at the same time lessens its toughness and absorbs moisture, and ought to be prohibited in England, as it already is in Germany. On the detection of adulteration of leather see *L.I.L.B.*, p. 212. Drum-stuffing is in this country mainly applied to shoe leathers, but in America, with the hot-air drum, is coming into increasing use for harness, and even belting.

A method of stuffing is used in Germany for heavy belting and the like which appears at first glance to contradict the axiom that leather must be stuffed wet. It is called *Einbrennen* (to " burn in "), and consists in first drying at a high temperature (50° C.) to ensure the absence of all moisture, and then either pouring hot melted tallow over the leather on a table and holding it over a brazier to allow the grease to sink in, or dipping it completely in a bath of melted tallow. The exception is only apparent, because, though the leather is at this stage completely saturated with tallow, it is only after wetting and drumming that it attains the flexibility due to true stuffing. Similar methods are applicable to alumed leathers, and even to chrome leather ; and so-called " waterproof " or " anhydrous " leather is made by immersing thoroughly dried leather in a bath of 2 parts of rosin and 1 of paraffin, or some similar mixture. If the leather is not first thoroughly dried, it is scalded and destroyed by the hot grease.

The most troublesome defect to which stuffed leathers are liable is known as " spueing," and is of two kinds, of which the first and less serious (perhaps more properly distinguished as " striking out ") consists of a white efflorescence rather like incipient mould, which is easily wiped off, but generally reappears. This is due to the crystallisation of the harder fats, and especially of the free fatty acids, on the surface of the leather, and is almost sure to occur in greater or less degree when the hard fats such as tallow or stearine are combined with a non-drying oil such as neatsfoot, or when soft fats are present in the leather. It is sometimes combined with actual mildew, from which it is rather difficult to distinguish, even under the microscope, and may be caused by fungoid plants, which not only mechanically expel the fats by their growth, but probably promote their rancidity and the separation of the crystalline fatty acids. It is at most only a defect of appearance, and does not in any way injure the leather. It was constantly present in calf-kid, from the neatsfoot oil used in finishing, and was in this case rather liked by the buyers, who for some reason regarded it as a proof of quality. A very similar appearance may be caused by the use of solutions of barium chloride, alum, or other mineral salts for weighting or other purposes ; but is persistent when the leather is held to the fire, while the crystallised fatty acids melt and disappear. The fatty acids are at once removed by a drop of benzene or petroleum spirit, but unaffected by water, while with water-soluble salts the reverse occurs.

The second form of spueing is of a much more troublesome character, and makes its first appearance as minute spots or pimples of resinous matter raised above the surface of the leather, which if removed generally reappear, and which may become so bad as to form a sticky resinous coating over the whole surface. The exuded matter consists of the oxidised products of oxidisable oils, but the cause of its appearance is not always easy to explain. The currier generally attributes it to adulterated oils, and it must be admitted that some oils almost invariably produce it, but it appears occasionally when only the purest and absolutely genuine cod oil has been used. It can only be produced from drying or semi-drying oils, which include all the ordinary fish oils and most of the vegetable seed oils, but can never arise from tallow or stearine, from mineral oils or vaseline, or from genuine non-drying oils, such as tallow, neatsfoot, sperm, or mineral oils, nor, probably, from rosin oil. It is favoured by causes which promote the oxidation of oils, such as moist heat with limited access of air, and by the presence of oxygen carriers, such as iron-salts in blacks, and possibly also by the presence of free acids. A large amount of free fatty acid in the oils themselves is suspicious, not only because the free acids oxidise more freely than the neutral fats, but because their presence is an evidence of the tendency to rancidity and change in the oil. It is also said to be caused by previous mildewing of the leather, and certainly often occurs where the grain has been rendered porous by bacterial action in the soaks, limes, or bates, probably from the greater quantity of oil absorbed by these parts. While it is easy to say which oils may possibly spue, there is no known chemical test which will foretell whether a given sample is likely to do so under ordinary conditions. Eitner[1] states that seal oil extracted at a low temperature is very liable to spue, but that when heated for a considerable time to a temperature of 250° to 290° C. it darkens in colour and loses the tendency. This is probably true of many other marine oils, and may be one cause of the frequent trouble with modern oils, many of which, especially the lighter coloured kinds, are extracted by steam at a temperature below boiling point. It is very probable that one effect of heating to a considerable temperature is to dehydrate and separate albuminous or gelatinous matters which are present in the fresh oils, and which probably increase their tendency to decomposition. Many of these substances separate as " foots " from oils during long storing, and such old oils are said to be less liable to spue than those of recent manu-

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[1] Gerber, 1880, p. 243.

facture. It is not easy to say why the oil comes in spots to the surface instead of remaining inside the leather. Probably some expansion of volume occurs with oxidation or by bacterial growth, and a pimple of oil once formed on the surface "dries" there, but still absorbs oil from below, which dries in turn, and so increases the growth. "Spueing" is apt to occur when goods have been mildewed.

If oxidisable oils are used upon leather they "dry" upon the fibre if they do not "spue," and if a sufficiency of non-drying constituents are not present at the same time the leather will ultimately become hard, and may even crack from hardening of the fibre. Mineral oils are not liable in this way to form a hard coating on the fibre, but as they are slightly volatile, though of very high boiling point, they may ultimately evaporate and leave the leather insufficiently nourished. From their low surface tension they have great powers of capillary penetration, as is witnessed by the way that lamp oils "creep" over the surface of the lamp, but they have less affinity for water than the more oxidisable oils, and probably do not combine so intimately with the leather fibre. They are probably better used in combination with other greases than alone. Their miscibility with water is greatly increased by the addition of sulphonated fish oils, and the writer has examined a sample of sulphonated oil containing 80 per cent. of mineral oil which emulsified spontaneously when poured into water. The admixture of solid paraffin with stuffing greases has the tendency to make the leather feel less greasy and drier than it otherwise would; and crude turpentine and rosin are said to have a still greater effect in this direction.

The water which is required for satisfactory stuffing may in some cases be introduced into the stuffing grease as well as into the leather. The effect of dégras is largely due to the water with which it is intimately mixed, and when dégras or sod oil is deprived of that which it naturally contains, by heating it to too high a temperature, either before or after its mixture in a stuffing grease, its efficacy is greatly lessened.

Fat-liquoring (pp. 273, 378) may be considered a special case of stuffing, in which the oil is very perfectly emulsified with a large quantity of water. In this way very considerable quantities of oil may be introduced into leather without giving it the least greasy feel. Egg-yolk contains about 30 per cent. of an oil chemically very like olive, but with a larger proportion of palmitin, and may be considered as a very perfect natural fat-liquor, containing also some albumen, which serves as "nourishment " for the leather. If a means of emulsifying olive, lard, or tallow oil (with the addition of a little palm oil) with albuminous matter as perfectly as in the egg could be discovered, the problem of an egg-yolk substitute would in all probability be solved. Milk and cream are also natural fat-liquors.

Emulsions are suspensions of one liquid in another, in which, being freely suspended, the globules always take a spherical form. If oil be shaken up with water a system of this sort is formed, but quickly separates, the oil floating to the surface, but under suitable conditions such mixtures may remain permanent. This is promoted by smallness of the globules. By sufficiently vigorous mechanical mixing tolerably permanent emulsions may be formed of oil and water alone, and the globules of butter in milk can be so broken up by the centrifugal emulsifier that cream will no longer rise on standing. Mere shaking is not the most efficient way of producing emulsions ; in the centrifugal emulsifier the mixture is forced out through a narrow slit between the edges of two discs, so that the oil issues as thin sheets, which break up into minute globules, and, on the small scale, a very effective appliance consists of a cylindrical vessel with a piston covered with fine gauze or perforated metal, through which the oil is forced in thin streams, preferably not of circular form, which also break up into globules (see p. 91).

While it is possible to emulsify oil and water simply, the process is much facilitated by the addition of some third substance which lowers the interfacial tension between the two liquids, or coats the globules when formed so as to prevent their subsequent coalescence, and usually both effects are combined. Soaps of various sorts are among the most usual and effective additions, and probably act in both ways, lowering the tension between the liquids, and coating the globules when formed. These soaps are not always added directly. All commercial animal and vegetable oils contain at least traces of free fatty acids, which are saponified by the addition not only of caustic alkalies but even of ammonia or alkaline carbonates, and where the oils are almost neutral, emulsification is greatly assisted by the addition to them of a little commercial oleic acid. With mineral oils, which are unsaponifiable, alkalies alone have little saponifying effect, and the addition of soaps in some form is necessary.

Almost any soap will assist saponification, and ordinary domestic soaps are often used, but for some purposes are undesirably alkaline. By the cold saponification process described on p. 427 perfectly neutral or even superfatted soaps are easily made from any saponifiable oil, and if sufficient excess of oil be used the soap dissolves at once to a fat-liquor. For many purposes of leather manufacture castor oil has been found particularly suitable. The quantity of soap used should not be too large ; 2 to 4 per cent. is generally sufficient, and larger quantities are less effective. Rain or steam water should be used, as the presence of the lime and magnesia salts of hard waters causes precipitation of insoluble soaps, which do not assist emulsification, and may make the leather sticky, or produce other ill effects.

Sulphated oils (p. 441) have come largely into use for producing emulsions. The earliest of these to be used was the "Turkey-red" oil of the textile trades, which is sulphated castor, and after neutralisation, generally with ammonia, is miscible with water in all proportions. Used alone, it produces nice soft leathers, though Eitner states that they are apt to harden and become tender with time, but generally it is used to emulsify other oils.

Other sulphated oils, however, are now more largely used, and especially sulphated fish oils have become an important article of commerce. These, as they are put on the market, are usually intended for direct application to leather, and especially to assist in retaining the colour of sole leather during drying, and they frequently contain a large proportion of mineral oil. For use in fat-liquors, however, it would be better to employ the sulphated oil alone, and mix the mineral or organic oils as desired. On the analysis of sulphated oils much has been written lately, and recent volumes of the *American Leather Chemists' Journal* and of that of the *S.L.T.C.* must be consulted.

In fat-liquoring chrome leathers, soap is an important constituent, not merely as promoting emulsification, but in fixing the basic tanning chrome salt, by forming with it an insoluble soap. The same thing may take place with alumina and other mineral tannages. It is very important that before goods are fat-liquored all the soluble salts should be removed by washing, or rendered insoluble by so-called "neutralisation," as otherwise they will bleed into the fat-liquor, and precipitate the soap in it as an insoluble sticky substance, which will adhere to the surface of the leather and render subsequent dyeing and glazing impossible.

Emulsion may be brought about by other means than those just described. Viscous substances such as dextrine, gums, and proteids such as albumen render emulsion easier, either by lowering the surface tension or by coating the globules, or by rendering them less mobile, and so less inclined to coalesce, and fine powders such as starch may also coat the globules. The starch of the flour used in tawing pastes and in the manufacture of "Crown" leather are useful in this way, though they are not directly absorbed by the leather, and some mineral powders have the same effect, but could not be used in fat-liquors.

CHAPTER XXVII

JAPANNED AND ENAMELLED LEATHERS

Though the information which can be given on the subject of this chapter is far from being either so complete or so reliable as might be desired, it seems best, in view of the present importance of the subject, to offer what is possible. For many years the manufacture in England was almost entirely in the hands of the " master japanners," who held the secret of the boiling of enamel, and who would brook little interference either from their employers or from the labourers whom they engaged to do the actual manual work, and who were quite ignorant of chemistry, and worked only by traditional and empirical recipes. The natural result was that no progress was made, and that the manufacture fell more and more into the hands of Germans and Americans, who were not hampered in the same way, and who had at the same time the advantage of a far more favourable climate. Even yet, though things are better than they were, we are living far too much in a region of trade secrets and empirical knowledge, which will not be swept away till the problem is seriously and openly taken up by the chemists.

Japanning consists in applying to the leather a coating of oil-varnish laid on in successive layers, and usually dried by heat. *Enamelling* is a term applied to precisely the same process when the leather is grained or boarded. Japanned is often styled " patent " leather, but so far as the writer is aware has never been *made* under any valid patent. Japanning is usually done on the flesh side and enamelling on the grain, but flesh-splits are often printed and enamelled.

The first mention of such an idea is in a patent taken in 1799 by Edmund Prior for painting leather with colours and boiled oil and finishing with oil-varnish. No mention is made of stoving. In 1805 a patent was taken by Mollersten for the application of a mixture of linseed oil, whale oil, horse-grease, and lampblack, and details are given of its application which are practically the same as those still in use, but a mixture containing fats and fatty oils could never have produced a usable japan, and as patent laws were much less exacting in those days, very probably these ingredients were simply given as a blind to conceal the secret. Apparently the first japanned leather was put on the market in 1822, while enamelled was not made till 1837. The next patent was in 1854 for details of manufacture, when the varnish ordinarily used was stated to consist of "oil, amber, Prussian blue, litharge, white lead, ochre, whiting, asphalt, and sometimes copal," and the use of indiarubber is claimed.

Any ordinary tannage of dressing leather can be japanned, but as little fat of any sort can be used in currying, the tannage should be soft and mellow for shoe leathers, and, on the other hand, for the thicker leathers used for harness the grain must be firm and not inclined to "pipe." An essential point is that the leather must not contain grease or fatty oil, which causes the japan to "throw off" or run unevenly, or dulls its lustre, and even traces of grease or oil brought in contact with the finished japan make it soft and sticky. The writer has known a case where contact with dyed and finished East India sheepskins used as lining ruined a parcel of dress-shoe uppers, though they showed no sign of greasiness, but were proved by analysis to contain 20 per cent. of sesame oil. The beam work should therefore be planned to remove as much natural grease as possible, but it has now become almost universal to degrease leather with solvents which is intended for japanning. For shoe leathers it is most important that the leather should not stretch, as otherwise the japan cracks and gapes in lasting, and therefore probably the bating or puering should be very moderate, if indeed simple deliming is not sufficient, since the more the elastin is removed the greater the tendency the leather has to stretch. The same points must be considered in chrome leather intended for japanning, and especially that of the absence of stretch.

Currying.—This is much like that of other leathers, and of course dependent on the nature of the goods, but here again all operations must be directed to remove stretch. The leather must be made as level in substance as possible, and for japan must be shaved very smooth, but for enamel this is less important, as the goods are fluffed or whitened before coating, and generally lightly buffed on the grain. The goods are set out thoroughly on a clean table, lightly oiled on grain with linseed oil, and either dried out or printed when dry enough. A "willow grain" is that usually given.

Dubbing containing any animal fat must be carefully avoided, but cod oil may be sparingly used, and on the Continent and in America dégras is generally employed. Fat-liquoring seems a likely way of getting softness with a minimum of suitable oil, but experiment is desirable as to the oils which may be safely employed and their quantity.

When dry, goods for enamelling are either fluffed or whitened, and if too hard they may be softened by sleeking on the flesh and lightly grained with cork-board on the flesh side.

In the United States many large hides are finished in dull-coloured enamels for upholstery. A very thin buffing is taken off the grain with the band-knife, which is often finished bright and smooth in colours for hat-sweats and the like. The upholstery leathers are probably printed before enamelling, and the grain is raised afterwards by boarding.

Japanning.—In the ordinary English process the goods are now nailed down on large boards, perhaps 6 feet by 8 feet, which fit into the stoves like drawers, and which are covered first with thick felt and then with brown paper. Before nailing on, any holes in the hides which the japan might pass through are patched with brown paper and glue. It is said that a coating of fullers' earth is sometimes given at this stage to remove the last traces of grease, but the writer has never actually seen it done, and it is probably quite unnecessary with benzine degreasing. Sometimes the leather is darkened by the application of a black or dark blue dye before japanning.

There is no secret about the actual application of the japan, which is (or used to be) done by labourers hired by the master japanner. The skins first receive a coat of a thick japan, laid on with a finely toothed sleeker (*raclette, railike*), and dried in the stove, and this process is sometimes repeated till the coating is sufficiently thick, when it is smoothed down with a pumice stone. This used to be done by hand with a stone shaped somewhat like a horn, but in Germany a rotating stone, carried on a double-jointed arm driven by belts and moved over the leather by hand, is usually employed, while the leather is supported on a stone slab.

The English drying stoves are mostly unventilated, and heated by a close gridiron of steam-pipes on the floor to a temperature which may be as high as 71° C. (160° F.). German stoves do not much exceed 60° C. (140° F.), but a portion of the drying is always done in the sun. Americans are said for special purposes to go as high as 93° C. (200° F.), in which case the leather is previously prepared with a solution of alum and borax, 2 oz. of each to the gallon. Drying is there also completed in the sun.

In the German and American methods the skins are usually stretched on frames, often fitted with screws or toggle-joints at the corners to admit of their expansion after the skins are stretched, instead of on boards. The skins are put on the frames damp, and often receive their first coat in this stage so that the damp, and the thick nature of the japan may prevent its penetration, while in others the skins receive a coating of size somewhat similar to that used on waxed calf. In Germany the first coats are often applied with a sort of spatula on a stone slab, but later coats are thinned with turpentine and applied with a broad brush (*queue de morue*). In France the preliminary coatings are applied on frames, but the finishing is on boards, and the goods are exposed to the sun after the coatings are so far dried in the stove as not to retain the dust. No exact statement can be made of the number of coatings applied, as the practice differs in different works and with different classes of goods.

Preparation of Japans.—The foundation of all japans is linseed oil, and with this and Prussian blue alone it is possible to make a good japan.

The purity of the oil is of the first importance, and it is conceded that Baltic and Belgian seed is the most suitable, most others being more or less mixed with other seeds grown at the same time. Russian linseed is generally mixed with a certain proportion of hemp, but it is doubtful how far this is disadvantageous, as hemp oil itself makes a very fine lacquer, and is much used for this purpose in Russia. The oil is best bought in large quantities from a reliable presser and stored in large tanks in a warm place, so that clear and well-settled oil is always available for boiling. It deposits at first a good deal of " foots," but if left in the tanks these gradually disappear or subside to a very small bulk, so that even after years the deposit is very small. The foots probably consist principally of water and a little mucilaginous matter emulsified with the oil.

Chemically, linseed oil consists for the most part of the glycerides of one or two highly unsaturated fatty acids, of which linoleic and linolenic are the principal. These have the same number of carbon atoms as stearic acid, but the former has two double links or pairs of unsaturated bonds and the latter three pairs (see p. 432). They are thus capable of absorbing much oxygen, and also of polymerisation, or the linking together of two or more molecules into more complex ones, thus giving rise to resinous products of which the constitution is not well understood, but which become more soluble in alcohol, and finally even in water as the oxidation proceeds. This change, and not evaporation, is what constitutes the " drying " of oils. By the limited action of oxygen, or more slowly of air, drying oils are converted into a sort of jelly, which is much used in the manufacture of linoleum, and which finally dries to a more or less hard varnish.

Boiling of Oils.—When linseed oil is boiled with certain substances called "driers" changes take place which make its drying much more rapid. These driers are all either themselves oxidising substances or carriers of oxygen, or both, and the effect of boiling is much more rapidly attained when air is blown through the boiling oil so as to keep the driers fully oxidised. Litharge and other lead compounds are the oldest driers, but they darken the oil and have some other disadvantages, and manganese compounds, *e.g.* peroxide, borate, and resinate, have also come largely into use, giving a much paler oil, though not drying quite so rapidly. Small quantities of the drier remain dissolved in the oil, and lead compounds sometimes cause tarnishing of the film through the action of outside causes. The use of manganese oxide was first suggested by Faraday for printers' ink.

In commercial oil-boiling, quantities of 2 or 3 tons at least are heated in a steam-jacketed pan to about 116° C. (281° F.) by steam at 35 lb. pressure for three or four hours, air being forced in at the pan bottom, and the driers (10 lb. per ton and upwards) are then added. Large quantities of pungent vapour (acrylic and croton aldehydes, etc.) are produced, which are carried to a furnace chimney, and the air becomes so far deprived of oxygen that a candle will not burn in it.

Air-blowing is not essential, and laboratory experiments can be made on so small a scale as on 50 c.c. of oil heated in a 150 c.c. beaker on a sand-bath.[1]

The aim in boiling for paint is to produce a film which will dry hard, but for japan it is necessary that the coat should remain elastic, or it will crack, *i.e.* the drying must stop slightly short of completion. In the older japans, litharge was generally used as a drier and filler, and it seems still to some extent to be employed in the United States. In Europe generally only Prussian blue (ferric ferrocyanide) is used, which seems at the same time to act both as drier and colouring agent. Very few accounts exist in literature of the actual preparation and composition of japans, and the writer, though at one time he had a good deal to do with the manufacture, never had the opportunity of following this part of the process, so that the best which can be done is to compare

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[1] *Cp.* F. H. Thorp, *Technology Quarterly*, 3, pp. 9–17, abstracted *J.S.C.I.*, 9, 1890, p. 628. Oil boiled with 0·4 per cent. of litharge at 250° (presumably Fahrenheit) for 2½ hours dried on glass in ten hours to a hard film, while with 1 per cent. of manganese borate heated for one hour to 230° it dried in twenty hours.

and collate the various information at our disposal and try from it to evolve a clear and connected scheme. Hennig[1] gives considerable detail, of which the following is an abstract. He advises very clear and old oil, and purifies (he states, from palmitic acid) by exposing to the sun in shallow trays on a 10 per cent. solution of ferrous sulphate. The clear oil is then heated to 50° to 60° C., and mixed with 25 to 30 grm. of red fuming nitric acid in large pots holding 30 litres, and provided with a series of holes one above another for racking, in which it is stirred for four days and allowed to settle, and the clear layer gradually drawn off, and filtered in a warm place through a paper previously saturated with oil. This purified oil, which already dries pretty quickly, is placed in a boiler of about double the capacity of the oil used, to allow for frothing, heated for an hour up to about 150° C., and 2½ per cent. of litharge added,[2] well stirred in, and the boiling is continued. Towards the end of the operation much pungent and combustible vapour is given off, which must be carried to a chimney. The oil is now allowed to cool and settle for two or three days in upright casks with taps 4 to 5 cm. from the bottom. "The lowest possible temperature promotes the settling of the palmitate of lead."

The clarified oil is now returned to the boiler, and a saturated solution of potassium permanganate is added at the rate of 2 grm. of the salt per litre of oil, well stirred till the mixture turns brown, and heated to 130° till all the water is driven off, when 7 to 10 per cent. of Prussian blue in the finest powder, sifted through silk, is dusted in through a sieve to prevent caking and thoroughly mixed, and the temperature is raised with continuous stirring till brown vapours are given off, the operation lasting two to four hours. When the sample draws in threads between the fingers on cooling, and makes a dark brown layer without greasy edges on writing paper, the boiling is nearly done, but may safely be continued a little longer. For very fine varnishes 3 per cent. of finely powdered gamboge may be added, and the boiling continued two hours longer at 150°. The lacquer is now allowed to cool slowly, and to settle for a week or two in a warm place. It is deep brown by transmitted light but deep black by reflected, and is a thick syrupy liquid

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[1] *Chemiker Zeitung* about 1878, reprinted in *Der Gerber*, 1878, p. 53, and in the *Leather Manufacturer*, 1892, p. 631.

[2] The quantity of litharge used seems unnecessarily large, not more than ½ per cent. being employed in ordinary oil-boiling. No details of time are given, or whether a higher temperature is used towards the end of the operation.

at ordinary temperature, but thin enough to flow from the brush when warmed.[1]

In the writer's own experience the oil underwent no previous preparation but long settling, and he has no reason to think that litharge was used, but a small quantity of "rose spirit" was added in the boiling, which was believed to brighten the japan. Rose spirit is one of the dyers' mordants, and is probably a mixture of tin chlorides and nitrates. For the first grounding japan a "common" Prussian blue of a paler colour, and containing a large proportion of precipitated alumina, was used, but for the later coats only pure Prussian blue of the best quality. The alumina no doubt served the purpose of a thickener or filler, and the writer's experiments with finely ground kaolin were quite promising. The final finishing varnish is the same as the japan, but with the addition of copal varnish, which is usually that sold by the varnish maker. Villon [2] recommends the following :—1 per cent. of finely powdered potassium bichromate is added to the oil at 100° C., retaining that temperature for half an hour, and then raising to 160°, adding 10 per cent. of Prussian blue, and boiling as described, and finally adding 30 per cent. of a copal varnish, made by heating 100 parts of boiled oil, 100 parts of gum copal, 100 parts of shellac, 300 parts of spirit of turpentine, and 25 parts of ceresine or mineral wax, in an autoclave to 350° for half an hour. Copal can only be dissolved by heating in this way. Copal varnishes are now largely superseded for japanned leather by solutions of nitrocellulose, which are much more elastic.

Davis [3] gives considerable detail of American processes of japanning, which appears to be gathered from a good source. The following is a summary, referring mainly to the large split hides used for upholstery, which have been already spoken of. The hides are stretched wet on frames, dried by heat with fan ventilation, taken off the frames, and softened by a "pin-block" machine, in which a head, something like that of a sole-cutting press, but studded with short rounded pins, comes down on a block with corresponding larger holes or grooves, and finally by boarding on a table. Any holes are then patched with paper and glue to prevent japan running through, and the hides, again

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[1] The addition of permanganate not merely oxidises, but furnishes a certain amount of manganese drier. Linolenic acid fully oxidised by permanganate yields tetrahydroxystearic acid. The object of the gamboge is not obvious, but its use is mentioned by other writers.

[2] Villon, *Traité pratique de la Fabrication des Cuirs*, Paris, 1889.

[3] Davis, *The Manufacture of Leather*, Philadelphia, 1897.

stretched on frames, now receive a heavy coat of "daub" or first japan, made as follows:—Raw linseed oil is boiled in an open pan over fire[1] for about twenty-four hours extending over two days, and being stirred continuously during boiling with a perforated iron paddle. During the first twelve hours it is gradually raised to a temperature of about 300° C., and is then allowed to fall to 200° before leaving for the night. On the second day it is again raised to 300° to 320° and cooked to a jelly, and again cooled to 200°, and the fire completely extinguished, and even the bricks cooled with water, and petroleum-naphtha up to about one-third of the volume of the oil is added and well stirred in, and this is repeated till about 1⅓ times the volume of the oil has been added, much of the naphtha being evaporated by the heat of the japan.[2] The workmen call this "sweetmeats," and it does not form daub till ½ lb. per gallon of good lampblack free from grease has been added and well mixed. The daub is applied with a steel slicker about ⅛ inch thick and 10½ inches long, well worked in, and the excess slicked off. It is then thoroughly dried in air or sunshine, and a second coat is given, which is dried in the stove at 45° to 50° C. For enamels two coats of daub suffice, but for smooth japans a third is generally given. Enamels now receive a "slicker-coat" boiled to about the thickness of treacle, and put on with a smaller and thinner slicker, and after drying about twelve hours in the stove are pumiced, and receive a coat of enamel varnish, which is made of linseed oil and about 2 to 6 oz. per gallon of "Chinese blue," and is boiled about eight hours, and thinned with naphtha to the same consistence as the slicker-coat. (The writer has not been able to ascertain definitely the composition of Chinese blue, but it is pretty certainly some form of Prussian blue.) The goods are again

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[1] Steam boiling is not practicable, from the very high temperatures required. Electrical heating would be possible.

[2] This apparently wasteful process is probably based on experience. Petroleum-naphtha is not a good solvent for the oxidised and polymerised oils of the japan, and if mixed at a lower temperature an emulsion rather than a true solution would result, though at a high temperature the two liquids are mutually soluble. The natural remedy would be to mix cooler, and again heat in an autoclave till solution took place, but with so volatile a liquid as petroleum-naphtha this would produce a very high pressure. Probably a more practical means would be first to dilute the japan with a "common solvent" such as turpentine, and then to add the naphtha. Common solvents are bodies which dissolve both the constituents to be mixed, and if added in sufficient quantity generally lead to their mutual solution. Thus a moderate quantity of alcohol will bring about the common solution of water and ether.

pumiced, and receive a final coat of the same varnish, and are dried in the stove at about 60° C., and exposed to the sun and air to remove stickiness.

The smooth japans receive two coats of "black varnish," with intermediate pumicing. "Black varnish" is made by boiling linseed oil with raw umber (containing ferric hydroxide) for eight to ten hours at 260° to 300°, $\frac{1}{4}$ lb. per gallon of which is carefully worked in, and it is thinned with naphtha till it will flow freely from a brush, with which it is applied. Two coats of this are given, with an intermediate pumicing and drying in the stove at 75° to 80°, and the last coat, after careful pumicing, is dusted first with a dry and then with a wet "sweep" to remove every trace of grit and dust. The leather is now ready for the finishing varnish, which is very similar to the enamel varnish already described, but perhaps boiled a little more, and thinned with naphtha till it will flow well from a brush, with which it is applied. Three coats are given, and dried for about forty-eight hours at 70° to 80° C.

The most important departures in modern practice from what has been described in the foregoing pages have been the use of nitrocellulose in japans, and especially in finishing varnishes, and the drying by the aid of ultraviolet light in place of exposure to sunshine. Both of these tend to minimise the handicap of the English climate, and there are manufacturers in this country who are already turning out products which can compete with those of the Continent, but naturally full information as to their methods is not available to the public.

The use of nitrocellulose solutions (celluloid) on leather is not new. So long ago as 1897 W. F. Reid in conjunction with Mr Earle took out a patent[1] for the enamelling of leather with a mixture of a low nitrated cellulose and nitrated castor oil dissolved in acetone. The proportions given in the patent were 11 parts by weight of nitrated oil and 5 parts nitrocellulose. About the same period Mr Reid showed the writer a pair of dress shoes he was wearing japanned with this material, which were bright and much softer and more elastic than ordinary japanned leather. Probably a smaller proportion of nitrated oil would have given a harder surface.

The cotton used for the purpose should be similar to that used for collodion. In many cases scrap celluloid can be bought which merely requires solution. The question of solvents is more difficult. For collodion a mixture of alcohol and ether is used,

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[1] W. F. Reid and E. J. V. Earle, Eng. Pat. 26677, 1897. *Cp.* also *J.S.C.I.*, 17, 1899, 972.

and for celluloid varnishes usually acetone and amyl acetate with some camphor, but during the war a variety of other solvents were used for "dopes" for aeroplane wings, and among others trichloroethylene, epichlorohydrin, chloroform, and other organic chlorine compounds, but these, though quite effective, have been largely abandoned, as their fumes were found very poisonous to the work-people. If used at all, very effective ventilation is necessary, which should be downward and away from the operatives, as the vapours are very heavy. A solution once made can frequently be diluted without injury with other solvents, such as alcohol, benzol, or petroleum spirit. Celluloid is soluble in acetone alone, but forms a viscid jelly rather than a true solution, and the addition of amyl acetate is necessary to produce a bright and coherent coating.

For some sorts of leather, where a very thin coating is desirable, it is probable that celluloid solution alone, with a small proportion of nitrated, or even of ordinary, castor oil, and either mixed with or applied above pigment colours, might be useful. In the United States pigment finishes for light leathers have come largely into vogue for covering grain and dyeing defects, and these seem sometimes applied with a celluloid medium and by spraying, though in other cases water solutions are used in a manner very similar to the sole leather finishes described on p. 368. The New Explosives Co. Ltd. at Stowmarket supply celluloid solutions suitable for such purposes, and could no doubt give much useful advice as to their use. They also, I believe, supply a small sprayer suitable for experimental purposes. Upholstery leathers sprayed with a celluloid varnish would be to a great extent waterproofed, so that they could be used for automobiles and the like.

As regards drying by ultraviolet rays, the usual method seems to be to carry the skins in frames, suspended from a slow moving chain or some similar device, past a battery of mercury lamps. These lamps must be blown in quartz, as glass is much less permeable to the ultraviolet rays. The arc is "struck" by allowing the mercury to flow from one bulb to another. A good pattern is made by the Thermal Syndicate Ltd., Wallsend-on-Tyne. Some care is necessary in their use, as the light is very injurious to the eyes, which should be protected by dark red glass in looking at the lamps, and the rays also produce unpleasant sunburns, especially on parts of the skin not usually exposed. It will be remembered that the light is often used by surgeons in extirpating malignant skin diseases.

Ultraviolet rays have a powerful ionising action on the air through which they pass, leading to the production of some oxidising substance generally supposed to be ozone, which has an injurious action on the leather, and several patents have been taken for its removal, especially one by Doerr and Reinhart of Worms, which cover the use of ammonia gas[1] in the drying chamber. A very competent manufacturer has expressed the opinion to the writer that the injurious vapours were not those of ozone but of oxides of nitrogen, and that, with sufficient ventilation, the difficulty was not a serious one. As the effect is produced by radiation and not by temperature, there seems no reason why the ventilation should not be as free as that of open-air drying, though experiments are desirable as to whether it might not be supplemented and quickened by heat applied in other ways.

The present mode of drying in hot unventilated stoves seems repugnant to common sense, since we have known the great part which oxidation takes in the process, and the drying would probably be more rapid and complete with better ventilation, even if the temperature were somewhat lower. Drying in "tunnels" in a current of hot air, the frames being carried on trucks, would seem worth trying where goods of uniform sort and size were manufactured (*cp.* p. 558). The process does not seem to be *wholly* one of oxidation, for glass lights and other cooler points in the stoves become coated in course of time with dark brown sticky matter.

As regards laboratory experiment much may be done. Small japan-boiling experiments may be made as described on p. 479, and experimental samples of japan, either on leather or on glass plates, may be dried in an ordinary water-oven regulated by a thermostat to the proper temperature, and though the same finish and smoothness may not be got as obtained in the works, it is at least possible to see whether the japan dries with a smooth bright surface, sufficiently hard, and yet not brittle. It would be interesting to try comparative experiments in boiling in closed flasks to observe the effect of oxidation, and perhaps drying under the same conditions might throw light on the question of ventilation. Different driers and mixtures should be tested. It is probable that precipitated hydric ferric oxide in fine powder might be substituted for the expensive Prussian blue, and ferric

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[1] The following patents may be referred to :—

U.S. Pat. 1099378, 1910.
Junghans, Eng. Pat. 10971, 1912. *J.S.C.I.*, 1912, 694.
Junghans, Fr. Pat. 443406, 1913. *Coll.*, 1913, 337.
Doerr & Reinhardt, D.R.P. 267524. *Coll.*, 1914, 41.

resinate and borate also suggest themselves. The use of very finely levigated ultramarine, especially in the bottom coats to correct the brown-black of the japan, seems also worth trial, as it is comparatively cheap, and would probably be unaltered by the boiling. When japanning was first introduced Prussian blue was probably the cheapest blue known, and the idea was to correct the brown of japans made with lampblack.

Cellulose acetate has been recently much used for "dopes" and varnishes, as well as for non-inflammable films, and is probably applicable in japanning.

CHAPTER XXVIII

DYES AND DYEING

Before the discovery of artificial organic dyestuffs the only colouring materials known to industry were those of mineral and direct organic origin, and on this account the dyeing of leather was formerly subject to great difficulties and limitations.

The discovery of the means of artificially preparing an organic dyestuff (mauve) by Perkin in 1856 opened up a new field for research, and since that time the list of commercial dyes has so increased, that there is now scarcely a tint or shade which cannot be accurately matched and reproduced by the coal-tar colours. These colours are often spoken of as "aniline dyes," owing to the fact that many of them, and especially the earlier ones, have been derived from aniline, one of the products of coal-tar; but more recently a considerable number of important colours have been prepared from other constituents of the tar, and it is therefore more correct to term the whole of the dyes obtained, either directly or indirectly, from coal-tar the "coal-tar colours."

The number of the coal-tar colours is now enormous, and their chemistry is far too complex even to touch upon here, and possesses a large literature of its own.[1] A large number will dye leather direct, while others must be mordanted like the dyewoods, and some are dyed in a colourless form, like indigo, and only develop colour on oxidation in the air. The variety of direct-dyeing colours is, however, so large, and their use so simple, that for ordinary leather dyeing there is little inducement to go beyond them. Some colours important for textiles are useless for leather, either as requiring too hot a bath or additions such as sulphide of sodium, which leather will not stand, and many colours much used before the war are no longer available. Mr M. C. Lamb, who is a well-known authority on leather dyeing, has, however, kindly contributed a list of suitable colours which can be obtained at present, but which, it may reasonably be hoped, will be extended in the near future. (App. C.)

The coal-tar colours are generally soluble in water or mixtures

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[1] As an introduction to the subject, *Artificial Dyestuffs, their Nature, Manufacture, and Uses*, by Ramsey and Weston (published by Routledge & Sons, Ltd., 3s. 6d.), may be recommended as cheap and as little technical as possible.

of water and alcohol, and the majority of them combine with the fibre of the leather without the use of any mordant, so that in most cases it is only necessary to apply a solution of the dye direct to the leather, though their suitability for the purpose varies considerably. A few which are only soluble in oils or hydrocarbons are not suitable for leather dyeing, though they may sometimes be utilised in conjunction with fats in currying or japanning; and there are also certain colours which are not applied to the fibre ready formed, but are developed on it by subsequent chemical treatment, and which have only been applied to a limited extent to leather.

A number of the coal-tar dyes, which are produced in the crystalline form, have a totally different colour when solid to that of their solutions and to the colour they produce when dyed. A well-known instance of this is magenta or fuchsine, which forms glistening green crystals, while in solution it is a brilliant red dye. The colours of the crystals are usually complementary to those of the solution; thus several blues have the appearance of metallic copper, and violets, such as methyl violet, are greenish-yellow, generally with a pronounced metallic lustre. This peculiarity is the cause of the defect in dyeing known as "bronzing," in which the dye, when applied in too concentrated a form, takes a surface shimmer of its complementary colour, and is utilised in "bronzed" leathers by applying the dye in a concentrated, and often alcoholic, solution.

The coal-tar colours are mostly either "acid" or "basic." The former are the salts of organic colour-acids with inorganic bases (generally sodium), and are usually readily soluble in water, but frequently do not fix themselves on the fibre till the colour-acid is set free by the addition of some stronger acid to the bath, and in many cases the free colour-acid is of different colour to its salts. The "basic" colours are salts of colour-bases (organic bases of the nature of very complicated ammonia derivatives) with acids (mostly hydrochloric, sulphuric, or acetic). Most of these in commercial use are soluble in water, though a few require the addition of alcohol. The colour-bases themselves are usually insoluble in water, and therefore precipitated by alkalies, and in some cases they are also colourless. The basic dyes have generally greater intensity of colour than the acid dyes, but large classes of them are very fugitive when exposed to light, and in strong solution many others are very liable to "bronze," a defect which is generally less marked with the acid colours.[1] Acid and

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[1] It has been shown by Lamb that many basic colours are much faster to light on leather than on textiles.

basic dyes cannot be employed in mixture in the same dye-bath, as they usually precipitate each other.

As it is not obvious at first sight whether a given dye is acid or basic, a reagent to distinguish them is useful. For this purpose a solution of 1 part of tannic acid and 1 part of sodium acetate in 10 parts (by weight) of water is conveniently employed, which gives coloured precipitates with basic dyes, but is not affected by acid ones. The fact that basic dyes are precipitated by tannins influences their use in leather dyeing, not only as regards their fixation on the leather-fibre by the tannin which it contains, but as the cause of their precipitation in the dye-bath if great care is not taken to avoid the presence of tannins in a soluble form, either by very thorough washing, or by fixation of the tannin by metallic salts, such as tartar emetic (*cp.* p. 498). The use of the sodium acetate is to combine with the mineral acid of the colour-salt, which if left free would prevent complete precipitation, by substituting acetic acid, which is much weaker, especially in presence of excess of sodium acetate (*cp.* p. 99).

In using the terms "acid" and "basic" with regard to dyes, it is not to be understood that the dyestuffs as employed are acid or alkaline in the sense that vinegar is acid and soda basic, but merely that the actual colour-constituent of the salt is in the one case of an acid nature, and set free by stronger acids, and in the other case is basic, and liberated (and often precipitated) by stronger alkalies.

There are several general theories [1] with regard to the fixation of colours in dyeing organic fibres, and it is probable that no one of them affords a complete explanation in all cases. One holds that the action of dyeing is mechanical rather than chemical, the colour adhering to the fibre by surface-attraction; another, that an actual chemical compound is formed between the dye and the dyed material or one of its constituents; and a third, the "solid solution" theory of Witt, is in a sense intermediate, holding that the colouring matter is actually dissolved in the dyed fibre. The idea of a solid solution, strange at first, offers little difficulty on consideration. The colouring metallic salts in tinted glasses exist obviously in solution in the melted glass, and can hardly be said to change their condition in this respect when the glass becomes solid. Gelatine, indiarubber, and perhaps all other colloid bodies, absorb water or other liquids without

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[1] Compare theories of dyeing with those with regard to tanning mentioned in Chapter XXXII. There is much in common between the two processes, and Zacharias has shown that many dyestuffs have also tanning properties.

losing their solid form, and these liquids may fairly be said to be dissolved in the solid. All animal and vegetable fibres are in this respect like gelatine, and during the process of dyeing are swollen with water. It is quite easy to dye a mass of gelatine throughout with most water-soluble dyestuffs. (Compare on these points what is said in Chapters IX. and X. on the physical chemistry of hide-fibre.) The distinctions between solution and molecular surface-attraction on the one hand, and certain forms of chemical combination on the other, are not wide ones, and probably all three theories are true in different cases, and shade off into each other by imperceptible gradations. The subject of leather dyeing is, in fact, a very complicated one, since we are not dealing with a fibre of uniform composition, but with one which has had its structure (both chemical and physical) altered by the processes to which it has been subjected during its conversion into leather.

Although, strictly speaking, the constitution of the gelatinous fibre of the skin is unknown, we are quite justified in stating[1] that, like the amino-acids which are important proximate products of its decomposition, it contains both acid and basic groups, and is therefore capable of attracting both bases and acids. It is well known, for instance, that neutral hide-fibre is capable of withdrawing sulphuric acid from a decinormal solution with such vigour that the residual liquid is neutral to litmus paper; and it will also absorb caustic alkalies with perhaps equal avidity.[2]

It is thus readily dyed by colouring matter of either basic or acid character, and in many cases will even dissociate their salts, dyeing the characteristic colour of the free dyestuff, but possibly at the same time fixing the liberated base or acid with which the colouring matter has been combined. Many tanning processes consist in a somewhat analogous fixation of weak bases and acids, and it is therefore to be anticipated that they will profoundly modify the colour-fixing properties of the original fibre, as indeed proves to be the case. Exactly what the result of a particular tanning process in this respect will be is less easy to foresee.

In the ordinary vegetable tanning process the tannins, which are of acid nature, are freely fixed by the fibre. It is, therefore, not surprising that vegetable-tanned leather most readily fixes the basic colours, especially as these form insoluble compounds with the tannic acids, so that it is quite probable that the dyeing is mainly effected by the formation of tannin-colour-lakes on the fibre, rather than by actual fixation of the colour-base in com-

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[1] Procter, *Journ. Soc. Chem. Ind.*, 1900, p. 23.

[2] *Cp.* Chapter X.

bination with the original matter of the skin. It is noteworthy, however, that even fully tanned skin has by no means lost its attractions for acid colouring matters, many of which will dye it even without the presence of free acid, though it is possible that the tannic acid performs the function of saturating the alkaline base with which the colour acid has been combined.

It should be pointed out that while the substance of animal skin consists practically of gelatinous fibres, it is covered on the outer surface with a thin membrane of extreme tenuity, called the hyaline or glassy layer (p. 56), which, in the living animal, separates the true skin from the epidermis. This layer, the chemistry of which is quite unknown, reacts to colouring matters differently from the gelatinous fibres, and probably is less absorbent for basic colours, and more so for the coloured anhydrides of the tannins, and perhaps for acid colours generally, than is the true skin. As a result it colours more darkly in tanning and less so in dyeing with basic colours, and as it is extremely liable to damage in the preliminary operations of removing hair and lime by the tanner, this irregularity of colouring is a serious disadvantage, which is most marked with the basic colours. Small quantities of lime left in the skin are also probably important causes of irregular dyeing.

Mordants are chemicals used to enable the fibre to fix dyes for which it would not otherwise have sufficient attraction, and hence are generally substances which have affinity both for the fibre and the dye. Thus cotton, which does not itself attract the basic colours, is mordanted for them by a solution of tannin, which it attracts, and which, in its turn, attracts and fixes the colours. In many cases, however, the function of mordants is more complex, not merely fixing the dyestuff, but often modifying, or even producing, its colour. Thus tannin dyes black on an iron mordant, though it is itself colourless. Such mordants may be applied *after* the colouring matter, where the latter has sufficient attraction for the fibre to be taken up alone, but does not produce the required colour. This process is often called "saddening," as the colour is generally darkened. A familiar instance is the use of iron solutions to darken or blacken tannin or logwood. There is scarcely any distinction in theory between mordants of this class and the constituents of dyes which are successively applied to the leather in order to produce the colouring matter on the fibre. Among these may be mentioned several mineral salts which were formerly employed in leather dyeing, though their use is now nearly obsolete. Iron salts are easily fixed by leather, whether tanned or tawed, and in the former case produce a dark colour by action of the tannin. On subsequent treatment with a solution of potassium ferrocyanide a deep blue is formed (Prussian blue). If copper acetate or ammoniacal solution of copper sulphate be substituted for the iron salt a deep red-brown ferrocyanide is produced. Yellows are sometimes dyed by first treating tanned leathers with lead acetate, which is fixed by the tannin, and then with potassium bichromate, by which yellow lead chromate is produced. A more important use of lead is in the so-called "lead-bleach," which is really a white pigment-dyeing with lead sulphate. The tanned leather, after washing, is first treated with a solution of lead acetate (usually "brown sugar of lead" of about 4 grm. per litre), and subsequently with a dilute sulphuric acid of about 30 grm. of concentrated acid per litre, and then thoroughly washed to free it from acid. The process is often used as a preparation for dyeing pale shades, as many of the aniline dyes are easily fixed on the bleached leather, but is subject to the disadvantage attendant on all pigments containing lead of becoming rapidly darkened by traces of sulphur or sulphuretted hydrogen, such as are constantly contained in lighting gas, or arise from the putrefaction of organic matters. The use of acid is also liable to cause early decay of the leather if not thoroughly removed.[1]

A large proportion of the coal-tar colours contain amino-groups (NH_2 groups) which, when treated on the fibre with nitrous acid (or an acidified solution of sodium nitrite), become "diazotised" (converted into $-N:N-$ groups with elimination of OH_2). On further treating the diazo-compound with solutions of amines or phenols, combination takes place, and new azo-colours are formed in or on the fibre, often remarkably fast to washing or rubbing. Since these qualities are less important in leather than in textiles, and the process is moreover somewhat delicate, and the nitrous acid is apt to affect the leather injuriously, these processes have been little used in leather dyeing, and are only mentioned here for the sake of completeness.

The use of the natural polygenetic colours in dyeing leather of vegetable tannage, which was once universal, is gradually disappearing, except for the production of blacks. Leather cannot be very satisfactorily mordanted for these colouring matters; but they have some natural attraction for the leather itself, and are generally dyed first, and their colours afterwards developed by metallic mordants such as iron, chrome, tin salts, and alum, which act not only on the absorbed dyestuff, but

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[1] Barium salts cannot be usefully substituted for those of lead, as they have no attraction for the tanned fibre.

frequently on the tannin and colouring matters derived from the tanning materials. For black dyeing the use of coal-tar colours, either alone or to deepen the colours produced by iron, is gradually extending. For suitable colours see App. C. As coal-tar blacks are mostly dark violets rather than dead blacks their colour may be deepened by the admixture of suitable yellows or browns, and this is frequently done by the colour manufacturer. Apart from the coal-tar colours, black dyeing is generally produced by the action of iron (and chrome), either on the tannin of the leather itself or on logwood. As the leather is frequently greasy, and the satisfactory formation of a tannin- or logwood-lake can only take place in presence of a base to absorb the liberated acid of the iron salt, the skins are either brushed with, or plunged in, a logwood infusion rendered alkaline with soda or ammonia, or the tanned leather receives a preliminary treatment with weak soda or ammonia solution. As such solutions act powerfully on tanned leathers, rendering them harsh and tender, great care must be taken to avoid excess. The effect of this alkaline treatment is not only to assist the wetting of the greasy surface, but to prevent too deep penetration of the dye, by causing rapid precipitation of the colour-lake. In recent times, however, leathers are sometimes demanded in which the colour goes right through, and in this case it might be well to reverse the treatment, beginning with a weak solution of a ferrous salt, perhaps with addition of sodium acetate or potassium tartrate, and finishing with alkaline logwood, as without alkali the full colour is not developed. The use of iron salts is not very satisfactory in regard to the permanence of the leather ; and in this respect it is of great importance that they should not be used in excess, and that any strong acids they contain should be saturated with permanent bases, and if possible washed out. Leather surfaces blacked with iron almost invariably ultimately lose their colour, becoming brown if tannins and red if logwood has been employed, and at the same time the leather surface usually becomes brittle or friable. This is to a large extent due to the effect of iron oxides as oxygen carriers. Exposed to light they become reduced to the ferrous state, oxidising the organic matters with which they are combined, and in the dark they re-oxidise, and the process is repeated. It is therefore of the first importance that excess of the organic colouring matter should be provided, and that the quantity of the iron should be as small as possible, and in stable combination. These points are greatly neglected in practice, especially where blacking is done by the application of iron salts without logwood, when the evils mentioned are intensified by the actual removal of part of the tannin of the leather, and perhaps by the combination of ferric oxide with the skin-fibre itself, forming a brittle iron-leather. Treatment with alkaline sumach-, gambier-, or logwood-solutions, both before and after the application of the iron, would lessen the evil. Iron-logwood blacks are much less permanent and fade more rapidly under the influence of light and air than iron-tannin blacks. The use of iron blacks on curried leathers seems considerably to increase the tendency to "spueing," a defect due to oxidation of the oils (see p. 469). Copper salts mordant logwood a very dark blue, which is much more stable than the iron compound, and hence are often used advantageously in mixture with iron salts. In practice, iron blacks are generally oiled in finishing, and this renders them more permanent, both by protecting the lake from air and by forming iron soaps which are stable. The use of actual soaps in blacking and finishing is not unknown, and probably deserves more attention. Hard soaps of soda and stearic acid[1] form an excellent finish where a moderate glaze is required, the soap jelly being applied with a brush very thinly, allowed to dry thoroughly, and polished with a flannel or brush, or glassed. Many acid colours are soluble in such soap jellies, which may thus be employed for staining. Similar but harder finishes, and capable of being glazed to a high polish, are made by dissolving shellac with dilute borax or ammonia solutions.[2] Both of these finishes are useful in lessening the tendency of iron blacks to smut or rub off, a failing which is due to the precipitation of loose iron lakes on the surface instead of in combination with the fibre, and is particularly obvious where "inks" or one-solution blacks are employed, or where the mordant and the colouring matter solutions are allowed to mix on the surface of the leather. Such "inks" are generally made with a ferrous salt and logwood or tannin, together with some aniline black, and the colour-lake should only be formed on oxidation. Chrome is not much employed in blacks with

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[1] One of caustic soda in 10 to 15 of water, boiled with 8 of stearic acid till clear, cooled to 25° C. and diluted with 400 to 800 water, with constant stirring, till a white jelly of suitable consistence is obtained. Somewhat similar, but harder, preparations may be made with waxes, or fatty acids still higher than stearic. Saponified Japan wax would probably produce a good glaze.

[2] Five parts of shellac digested warm with 100 water and 3 of ammonia fort., or 1 of borax. If the solution is used as a "seasoning" for glazing, the waxy matter which separates on standing should be mixed by shaking before use. As a varnish, a stronger solution should be used and the wax skimmed off.

vegetable tannages, as it only produces blacks with logwood, the chrome compounds of tannins having no colouring value, and bichromates being very injurious to the leather if used at all freely.

In dyeing blacks on other than vegetable tannages, however, chrome becomes of importance, as logwood is principally employed, though sometimes in conjunction with tannin, and often with addition of quercitron or fustic, to correct the bluish shade of the logwood-chrome or logwood-iron lake. It must not be overlooked in practice that if ferrous salts are mixed with bichromate solutions the latter are reduced and the iron is oxidised to the ferric state.

In alumed leathers the fixing power of the original hide-fibre is much less affected than in vegetable tannages. Whatever may be the truth with regard to the latter, there is little doubt that physical influences are at least as important as chemical ones in the production of mineral tannages.[1] The amount of the tanning agent absorbed is greatly influenced by the concentration of the solutions, and in ordinary alum tawing much of the alumina may again be removed by free washing, especially immediately after tawing. In this case the sulphate of potash present takes no part in the operation, but both the alumina and the acid are absorbed, apparently independently. Alum or alumina sulphate alone is incapable of producing any satisfactory tannage without the assistance of common salt, without which the quantity of alumina absorbed is small, and the fibre becomes swollen by the action of the acid. In presence of salt the absorption is greater, and the swelling is prevented. The explanation of this is not to be found in the formation of aluminium chloride, for though this undoubtedly takes place, it has been shown that the action of aluminium chloride without salt is not more satisfactory than that of alum. It has long been known that salt prevents the swelling action of acids on skin, although it does not lessen the absorption of acid ; and the fact is capable of explanation on modern osmotic theories (*cp.* p. 121). The skin so treated is found to be converted into leather, but if the salt be washed out the acid is retained by the skin, which returns to the state of acid-swollen pelt. It is probable, therefore, that although the acid and alumina are absorbed in equivalent proportions to each other they are really dissociated and attached to different groups in the gelatin molecule, and that the effect of the salt is to allow the absorption of the acid without swelling, and, osmotically, to increase the dissociating power of the pelt. If, in

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[1] *Cp.* Chapter X.

place of a normal alumina salt, a basic salt is employed, such as may be obtained by partial neutralisation of the sulphuric acid with soda, satisfactory tannage may be accomplished without salt, a basic compound is absorbed, and the leather is much less affected by washing. In the analogous case of chrome tannage this basic compound may be still further deprived of its residual acid by washing the tanned skin with alkaline solutions, leaving a leather which is extremely resistant even to hot water ; and a somewhat similar result may be obtained with alumina, though with more difficulty, as apparently a very small excess of alkali destroys the qualities of the leather (*cp.* p. 272).

The results on dyeing are almost what might have been foreseen. While ordinary alumed leather absorbs both acid and basic dyes readily, the basic chrome leather has practically lost its affinity for the latter. Both chrome and alumina leathers readily absorb vegetable tannins, thus supporting the view that the acid-fixing groups of the gelatin molecule are still unsaturated (tannins are capable of tanning pelt swollen with sulphuric acid, and apparently of expelling the acid). In the case of chrome leather the effect of re-tanning with tannins is greatly to lessen its stretch and, if carried too far, to destroy its toughness, but it at once becomes capable of fixing basic dyestuffs. This property is frequently made use of in dyeing, but the effect on the leather must not be disregarded where softness and stretch are important, as in the case of glove-leathers. Polygenetic dyes are, of course, fixed on alum or chrome leathers by the alumina or chrome mordant, though apparently the bases are not present in the most favourable condition for fixing colours. Thus logwood extracted without alkali dyes vegetable-tanned leather yellow, alumed leather violet-blue, and chrome leather blackish-violet, and some of the alizarine group dye very well on chrome, as its resistance to hot water allows much higher temperatures to be used than with most other leathers. The tannin contained in dyewoods has the effect of lessening the stretch of chrome leathers, but at the same time gives them a "fuller" feel.

Something should perhaps be said on the dyeing of oil and aldehyde leathers, but the subject has as yet been scarcely treated scientifically, and our practical knowledge of the subject is insufficient to justify theorising (see, however, p. 461). Wash-leather which has been bleached with permanganate (p. 459) can be dyed pretty readily with most dyes, and if brown shades are required it is not necessary to remove the manganic oxide formed.

Defects in the colour of the finished leather are due to a variety of causes, but many are produced by want of cleanliness and system during the dyeing itself. The greatest care is needed in this respect, and in brush-dyeing a different brush should be used for each different colour, as it is impossible to remove thoroughly all traces of dye by the ordinary methods of cleansing.

Irregular and surface dyeing sometimes occurs owing to too rapid fixation of the colours, while in other cases the affinity of the dye is too small to allow of reasonable exhaustion of the bath. Addition of salts of weak acids, such as potassium hydrogen tartrate (tartar), or of those like sodium sulphate, which form hydric salts, lessen rapidity of dyeing with acid colours, while acids generally increase it, and it is also often increased by addition of common salt, which lessens the solubility of the dye. Weak acids, such as formic, or acid salts, such as sodium bisulphate, are generally to be preferred to sulphuric acid as an addition to the dye-bath,[1] and if the latter is used, great care is desirable in its complete removal. There is no doubt that the rapid decay of leather bookbindings and upholstery is largely due to the careless use of sulphuric acid in "clearing" and dyeing the leather;[2] and even if it is fully removed, it has saturated all bases such as lime, which are naturally present in leathers in combination with weak acids, and which would otherwise act as some protection from the sulphuric acid evolved in burning coal gas. A bath containing the salt of some strong base with a weak acid such as sodium acetate or potassium tartrate, used after dyeing, would lessen both these dangers.

"Bronzing," the dichroic effect produced by light reflected from the surface of many colouring matters, complementary to that transmitted by them and reflected by the surface of the dyed material, is not peculiar to basic colours, but is generally more marked in them than in acid ones. Basic colours, from their great affinity for tannins, and consequent rapid dyeing, are apt to dye irregularly, and without sufficiently penetrating the leather, and if the soluble tannin is not wholly washed out of the skins previously to dyeing, it bleeds in the dye-bath, and precipitates insoluble tannin lakes, which waste colour and adhere to the

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[1] See Report of Committee of Society of Arts on Bookbinding Leathers 1901.

[2] For most acid colours acetic acid has proved too weak to bring out their full colouring, but formic acid is quite satisfactory. If sulphuric acid is used, a weight equal to that of the dyestuff is sufficient.

surface of the leather. The inconvenience of basic colours due to their too rapid fixation may sometimes be lessened by slight acidification of the dye-bath with a weak acid, such as acetic or lactic. The acid may be still further "weakened" if desired by the addition of its neutral (sodium) salt. The precipitation of tannin lakes in the bath may be prevented by previous fixation of the tannin with tartar emetic, with titanium potassium oxalate or lactate, or some other suitable metallic salt (see p. 492).

The fading of the colours of dyed goods by exposure to light is a defect which has been much more investigated in the textile industries than in leather manufacture, though in the latter case, and especially with regard to bookbinding and furniture leathers, it is of even greater importance. It is probable that no colours are actually unaffected by strong sunlight, but in many cases the action is so slight that it may practically be disregarded, some of the coal-tar colours, and especially some of the alizarines, being practically permanent, while others, and particularly the aniline colours belonging to the triphenylmethane group, such as magenta, are so fugitive as to be practically bleached by a week of strong sunlight. Chrysoidine and the eosins are also very bad in this respect. The fastness of colours to light is a good deal influenced by the material on which they are dyed, and but little has been published of the results of direct experiments on leathers, but Mr M. C. Lamb has carried out a research of this nature,[1] and the subject is now receiving a good deal of attention in other quarters. Experiments are easily made by exposing samples to sunlight under glass or in a south window, a part of the leather being covered with wood or thick brown paper for comparison. The results are often complicated by the tendency of all leathers tanned with tannins of the catechol group, and especially with turwar (*cassia*) bark (p. 329), mimosa and quebracho, to darken and redden in sunshine, or even by exposure to diffused light. Pure sumach tannages are nearly free from this defect, and are also much less easily destroyed by the action of gas fumes (sulphuric acid) and the other injurious influences to which books and furniture are often subjected.[2]

Want of fastness to friction or rubbing is a defect generally more important in textiles than in leather, where it is usually prevented by glazings or other finishes applied to the surface, but in some cases, and especially in black leather, it is apt to be annoying. If suitable colours are used, the defect is generally

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[1] See *Journ. Soc. Chem. Ind.*, 1902, pp. 156–158.

[2] *Cp.* Report of Society of Arts Committee on Bookbinding Leathers, 1901.

due to the precipitation of loose colour on the surface, either by the too free use of mordants, or the dyeing of basic colours on leathers which have not been sufficiently freed from loose tannin. It is also often caused by " flaming," or the application of colour mixed with the " seasoning " used in glazing to hide imperfections in the dyeing or vary its colour. Colour applied in this way is only mechanically fixed on the leather, and is easily removed by moisture, staining articles with which it comes in contact.

A very similar defect may be caused by incomplete washing of the dyed leather, which leaves loose dye from the dye-bath in the goods. To avoid it in glove-leathers, where its occurrence would be particularly annoying, the natural mordant colours are still largely in use, which being precipitated on the fibre in an insoluble form by the mordant or " striker " (generally a metallic salt) are little liable to come off. Basic colours may be fixed by a subsequent treatment with tannin, or by topping with certain acid colours such as picric acid. Some few colours, and especially Martius or " Manchester " yellow (dinitronaphthol), are volatile at a low temperature, and therefore liable to " mark off " or stain any materials with which the dyed fabric, even in a dry state, is placed in contact, and some of these colours are also irritating to delicate skins. Many tans (gambier, etc.) also " mark off."

The practical dyeing of leathers varies considerably according to whether they are tanned with vegetable materials, chrome, alumina salts, or by chamoising. Vegetable tanned leathers are dyed either by hand in the " dye-tray " or in the drum or paddle, the two latter methods being now largely employed. The dye-tray is a shallow vat, about 10 inches deep, and large enough for the goods to be laid flat in it. In the English method one or two dozen skins, or even more, are dyed at a time, being turned over in the tray by hand, the undermost pair being drawn out and placed on the top (fig. 109). The method is convenient where only a small number of skins are to be dyed to one particular shade, which is more easily matched as the goods are always under observation, and it has the further advantage that, if desired, the grain sides only of the skins can be coloured, by " pairing " or " pleating " them before dyeing. For this purpose two skins of equal size are laid together flesh to flesh (pairing), or each skin is doubled down the back, flesh side in (pleating), and pressed firmly together with a sleeker on the table, when the skins adhere so closely that if carefully handled no colour penetrates between them during the dyeing, except a little round the edges. This effects considerable economy of dyestuff, as the fleshes would absorb a good deal, and for some purposes an undyed flesh is preferred. In dyeing in the paddle or drum the skins are merely placed loose in the dye-liquor, so that the fleshes are dyed equally with the grain sides. Paddle-dyeing has the advantage of effecting a considerable saving of labour as compared with the dye-tray, in which constant handling, which often lasts an hour or more, is required. It also allows of almost equal facility in examining the colour of the skins, which is very important when dyeing to shade; but it is less economical in dyestuff, as not only the flesh sides are dyed but a much larger volume of liquor is used, and as the dye-bath can never be entirely exhausted, more dye is run away in the used liquor. Drum-dyeing is much less expensive in this respect, as the volume of liquor may be very small, and from the efficiency of the motion the dyeing is very thorough, and penetrates deeply into or through the skin, which in many cases is advantageous, but it is difficult to dye to exact shade, since the skins can only be examined by stopping and opening the drum. Most dyes are more readily fixed at high temperatures, and in this respect the drum has an advantage over all other methods, as once heated it retains its heat with very little loss to the end of the operation, while both

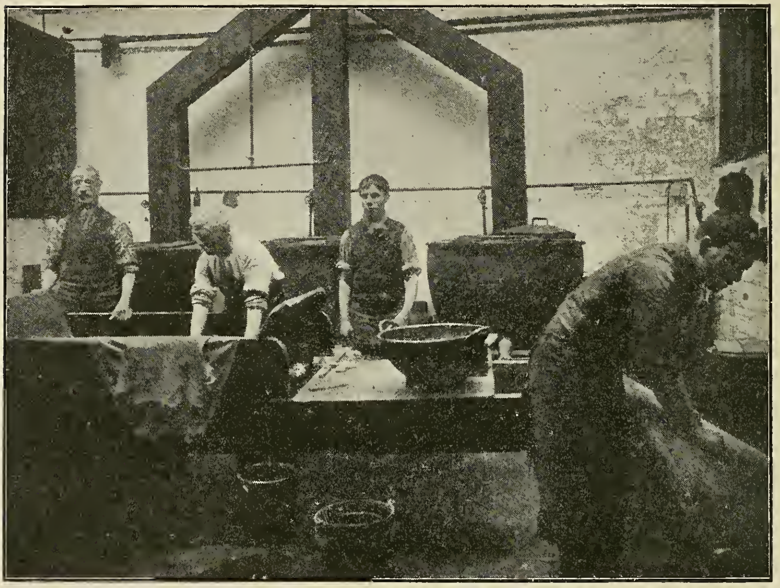

FIG. 109.—Dyeing in the Tray.

in the paddle and the dye-tray the liquor is rapidly cooled, and special methods of maintaining the temperature complicate the apparatus, and require great care to avoid overheating. It is usually best to work at the highest temperature which the goods will safely bear, and this varies to some extent with the class of goods, chrome tannages and chamois leather being peculiar in standing almost any temperature short of boiling. With vegetable tanned leather 50° C. may be taken as a maximum, but cold wet skins may safely be introduced rapidly into a liquor heated to 60°, as they will cool it sufficiently.

The Continental method of dyeing in two trays may be mentioned here, as it produces very rapid and even dyeing, with considerable economy of dyestuff, and the principle is capable of application to other methods where a large number of skins have to be dyed to the same colour. As generally carried out two trays are employed, each about 4 feet long, 18 inches wide, and 10 inches or a foot deep, and these are usually made with a sloping bottom, or propped up in such a way that the dye-liquor all runs to the farther side of the tray. A single pair of skins is usually dyed at once (in about 6 litres (5 quarts) of liquor for sheep and goat). To begin with, the first tray is filled with a very weak liquor, and the second with one of about half strength. The goods are entered in the first tray, turned a few times, and passed into the second; the liquor in the first is run away, and it is refilled with one of the full strength, to which the goods are then transferred and dyed to shade. The second tray is much reduced in strength by the skins, and now serves as the weak liquor for a fresh pair, which in its turn passes into that from which the goods have been dyed out, and then into a new liquor, each pair of goods thus passing through three baths, of which the last is of full strength, and which quickly brings up a full and even colour. In the ordinary English method the goods must, for the sake of economy of dyestuff, be dyed out in a nearly exhausted bath, which is a tedious operation, the last stage of dyeing often taking a time far longer than that required to bring the goods nearly up to shade, and even then failing to produce a good and full colour. This evil may be lessened by adding the dyestuff in several successive portions as the bath becomes exhausted, but cannot be altogether avoided with a single tray if any reasonable exhaustion of the bath is to be attained. At first sight it seems a very slow process to dye the goods in single pairs, but this is to a great extent compensated by the rapidity with which they take on colour. On the other hand, the solutions must be of considerable strength to avoid undue loss of time. In the Continental system the dyes, mostly of the coal-tar series, are used as strong solutions, and each new dye-bath is made up by filling the tray with a definite volume of hot water and adding a measured quantity of the dye-solution.

The re-use of partially exhausted dye-baths is generally limited to cases where either single dyes or mixtures of very equal affinity for the leather are employed, since where dyes of unequal affinity are employed one is more rapidly removed than the other, and the shade of the dye-bath is altered. Many dyes sold as single colours are really mixtures,[1] and alter in shade if successive quantities of leather are dyed in their solutions. Basic dyes are also apt to be precipitated by traces of tannin washed out of the goods, and thus rendered unfit for use a second time. This may be avoided by suitable preparation of the goods (see p. 503).

Much of the success of practical leather dyeing depends on proper selection and preparation of the goods. Sound uninjured grain is a matter of first importance ; no satisfactory dyeing can be expected on skins which through carelessness in soaks, limes, or bates are tainted by what is known as "weak grain," caused by destruction or injury of the delicate hyaline layer, which forms the natural glaze and outer surface of the skin (p. 56). For such goods "acid" are to be preferred to "basic" dyes, the latter having an especial tendency to dye darker and deeper where the grain is imperfect. Goods of different tannages and colours should never be dyed together, as they are certain to produce different shades in the same dye-bath. Tanned skins which have been dried, especially if they have been in stock for some time, should be thoroughly softened by soaking in tepid water and drumming, a temperature of between 40° and 45° C. being most advantageous. Skins, such as calf, of mixed or bark tannage, must now be freed from all bloom by scouring with brush and if necessary with slate or stone, but great care is requisite to avoid injury to the grain. A little borax or other weak alkaline solution assists in removing bloom. Fresh sumach-tanned skins merely require setting out with a brass or vulcanite sleeker, but those which have been long dried often dye more evenly and readily if they are re-sumached.

Dark-coloured tannages, such as Australian bazils, and East India sheep and goat tanned with cassia bark, are always im-

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[1] Such mixtures may often be detected by putting a drop of their solution on blotting-paper, when the dyes form differently coloured rings according to their more or less rapid fixation by the paper, or by dusting the dry dye *very* thinly on wet blotting-paper, when each particle produces its separate spot.

proved by sumaching, and if for light colours, by first stripping a portion of the original tan by drumming for a quarter of an hour with a weak ($\frac{1}{4}$ per cent.) solution of soap powder or borax at a temperature of 30° to 35° C. and then passing (after well washing in warm water, but with as little exposure as possible to the air) through a weak sour of sulphuric acid of 1 to 2 per cent. The acid should now be as thoroughly removed as possible by washing in water, and the goods should be sumached. The process, and especially the use of sulphuric acid, is always deleterious to the skins, and is one of the causes of the early decay of coloured bookbindings and furniture leathers. Formic or oxalic acid may be substituted for sulphuric with greater safety, and the risk of injury from sulphuric, which generally is only apparent after the lapse of a considerable time, is a good deal lessened by adding to the sumach liquor a small quantity of potassium tartrate, sodium acetate, or lactate, or some other salt of a weak organic acid, which is thus substituted for the much more dangerous sulphuric. Except in cases of absolute necessity for the production of light shades the use of sulphuric acid should not be resorted to, and then only for goods which are not expected to possess great permanence. For light shades for bookbinding and upholstery good sumach-tanned leathers and organic acids only should be employed. Alkaline treatment also demands great caution, as excess of strong alkalies is very injurious to the leather. Another objectionable method for the preparation of leather for very light shades is the use of the lead-bleach described on p. 492.

The sumaching is best done in a drum at a temperature of about 40°.[1] Lamb advises that 1 to 2 lb. of sumach per dozen is sufficient for calf, and recommends running in this liquor for two or three hours. The skins are then rinsed in water to free them from adhering sumach, and set out on a table with a brass sleeker, and are now ready for dyeing with " acid " dyestuffs. If " basic " dyes are used, thorough washing in several tepid waters is necessary to free them from the loose tannin ; and if deep colours are to be dyed, it is better, instead of too much washing, to fix the tannin, which then serves as a mordant for the colour. For blues, blue-greens, or violets this is done with a solution of " tartar emetic " (antimony potassium tartrate, of 5 to 20 grm. per litre according to the amount of tannin to be fixed, often with addition of some common salt), which produces

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[1] Caution is required in drumming in this and other stages, as the grain of tender skins is easily weakened by mechanical friction, leading to uneven dyeing.

no alteration in the colour. For browns, yellows, deep reds, or yellow-greens it is advantageous to use titanium-potassium lactate or oxalate (2 grm. per litre), which in combination with the tannin produces a very permanent yellow coloration on which the basic colours dye freely. In many cases the titanium salt is best applied after dyeing with one of the dyewoods (Dreher).

The basic colours usually require simple solution in hot water before adding to the dye-bath, and are used in quantities of 0·5 to 2·5 grm. per litre of dye-bath, according to their colouring power, which varies a good deal, and to the depth of shade required. The solutions should not be boiled, and some colours are injured by too high a temperature. Some colours dissolve incompletely, and require filtration through a cotton cloth. As basic colours are precipitated by calcium carbonate, it is important that " temporary " hard waters should be neutralised with acetic or lactic acid till they faintly redden litmus ; and in the case of colours which, from their attraction for the leather fibre, dye too rapidly, and consequently unevenly, better dyeing is often obtained by the use of a small excess of acetic acid, which also increases the solubility of the colour. Too much acid, however, will prevent the proper exhaustion of the bath. Some few colours, now little used, require to be dissolved in the first instance in a little methylated spirit ; and the addition of spirit will often assist dyeing and staining where the leather is slightly greasy, though considerations of cost generally prevent its use. Sodium sulphate is not unfrequently added to dyeing baths to improve equality of dyeing ; and with some of the cotton dyes common salt is used to lessen their solubility and facilitate the exhaustion of the dye-bath.

" Acid " colours usually need the addition of acid to the dye-bath to liberate their colour acids, and for this purpose sulphuric acid is generally used in weight about equal to that of the colour used. Its use is, however, objectionable in this case for the same reasons as in bleaching, since it is impossible by mere washing to remove it entirely from the leather, which it ultimately rots when concentrated by exposure to a dry atmosphere or high temperature, and it is better to use formic acid to the extent of two or three times the weight of the dyestuff. Sodium acid sulphate may also be used, but is probably more objectionable than an organic acid. Many acid colours, however, dye quite satisfactorily from a neutral bath. The acid colours are used in somewhat similar quantities to the basic, but are generally inferior in colouring power, though they dye more evenly, especially on defective grain, and are often more permanent to light.

Mention has already been made of the polygenetic or mordant dyestuffs which are still used to some extent for dyeing glove-leathers, and of which logwood is important in dyeing blacks. Fustic and Brazil-wood (peach-wood) are not quite gone out of use among old-fashioned dyers, even for dyeing moroccos and other coloured leathers of vegetable tannage. Peach-wood with a tin mordant (generally a so-called " tin spirits," made by dissolving tin in mixtures of hydrochloric and nitric acid) was formerly much used in dyeing cheap crimsons, but is now quite displaced by the azo-scarlets.[1] The acid tin-solutions were frequently very injurious to the leather.

The wood-infusion, rendered slightly alkaline with soda, ammonia, or, formerly, with stale urine, is usually dyed first on the leather, and followed by the mordant " striker " ; ferrous or ferric solutions, and potassium bichromate being used for dark colours, and tin salts, or sometimes alum, for the brighter ones. The mordant is sometimes added to the dye-bath towards the end of the operation, but is better used as a separate bath, as it is apt to produce a precipitate of colour-lake on the surface of the skin, which rubs off on friction. In some cases, and especially in black dyeing, the strong infusion of dye-wood and the necessary " striker " are successively applied by brushing instead of in the dye-tray.

Logwood and Brazil-wood are both Cæsalpinias closely allied to divi-divi. Logwood is *Cæsalpinia Campechianum* (see p. 329). Its colouring matter is hæmatoxylin, a substance nearly allied to tannins, and almost colourless ; which on oxidation gives hæmatin, which dyes directly a yellow-brown, only developing other colours by the aid of mordants. Logwood chips are extracted by boiling or heating under pressure for some time with water ; and as hæmatin gives dark purplish-red compounds with alkalies, soda or stale urine is frequently added under the mistaken belief that it produces a better extraction, but it really leads to waste of colouring matter by oxidation. It is best to extract with water alone, and add any necessary alkali to the infusion before use. One to 2 lb. of wood per gallon is frequently employed in making the infusion, and as this proportion of water is quite insufficient to properly extract the wood, the residue should be boiled with one or more further quantities, which are employed in turn for extracting fresh portions of wood. Logwood

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[1] Azo-colours are easily reduced and bleached by metallic zinc, and the writer once experienced considerable trouble from " galvanised " bolts used in the fittings of a copper bath, and zinc if used at all should be protected by varnish or japan.

dyes best at high temperatures, and especially in the case of chrome leather, with which a temperature of 80° C. may be safely used. The presence of a trace of a salt of lime is advantageous, and with very soft waters a little lime-water or chalk may be added to the logwood liquor. Logwood extracts, being principally used for blacks with iron mordants, are frequently adulterated with tanning substances.

In blacking skins the strong infusion is rendered slightly alkaline with sodium carbonate or ammonia, and brushed undiluted on the leather. If employed as a bath a somewhat weaker infusion is used, and the leather is frequently treated first in an alkaline bath to which a small quantity of potassium bichromate is often added. The object of the alkali is not only to assist in the formation of the colour-lake, by saturating the acid set free from the iron salt used as a striker, and thus to prevent the colour from penetrating the leather too deeply, but at the same time to overcome the resistance to wetting caused by grease or oil which the leather may contain. It is possible that in some cases sulphonated oil soaps might be used with advantage. Alkali must thus be used more freely when stuffed leather is to be blacked, but excess should be carefully avoided, as it easily renders the leather tender and brittle. The potassium bichromate oxidises the hæmatoxylin, or the ferrous salt subsequently applied, and forms a nearly black chrome-logwood lake. Bichromates must be used with great caution, as they tender the grain, and render it liable to "gape" in subsequent stretching.

The iron solution is generally either of ferrous sulphate of perhaps 5 per cent. strength, or commercial "iron-liquor," which is a "pyrolignite" or crude acetate of iron, containing catechol derivatives and other organic products from the distillation of wood, which act advantageously, both as antiseptics and in preventing the rapid oxidation which occurs when pure ferrous acetate is used. Iron-liquor is generally to be preferred to ferrous sulphate ("green vitriol"), as the sulphuric acid of the latter, unless completely neutralised by the alkali employed in preparation, acts in the end disastrously on the leather. Commercial iron-liquor is often adulterated with ferrous sulphate, which may be detected by its giving a precipitate with barium chloride. Great care should be taken not to use iron in excess of the logwood or tannin present, as it otherwise takes tannin from the leather itself, making it hard and liable to crack, while any uncombined iron acts as a carrier of oxygen, giving up its oxygen to the colouring matter or tannin with which it is in contact, and again oxidising from the air, and so causing "spueing" or oil-oxidation and other evils. The black colour-lakes are formed only with ferric iron, and if ferrous salts are used, they must be allowed to oxidise in the air after dyeing.

Good blacks which are more permanent than those with logwood may be obtained by merely treating leather containing an excess of oak-bark tannin or sumach, first with an alkaline solution (not at the most stronger than 2½ per cent. of liquid ammonia, or 5 per cent. of soda crystals), and then with iron-liquor. If it is not certain that the leather contains excess of a suitable tannin, a tannin solution must be employed like the logwood infusion, or the leather must be sumached. The addition of some sumach to logwood liquor is often advantageous, and a blacker (*i.e.* less blue) black, especially on alumed leathers, is obtained by using a proportion of fustic. Solutions made by boiling 10 per cent. of cutch with 5 per cent. of sodium carbonate give good blacks with iron-liquor and do not make the leather tender, and they can be used in mixture with logwood. Many commercial logwood extracts contain chestnut-wood extract as an adulterant.

Instead of dyeing in the bath it is very common, especially for the cheaper leathers, such as linings and coloured leathers of the commoner sort, to apply the colour by brushing (commonly called "staining"). Many colours, however, which dye well with time and warmth are inapplicable in this way, and only those should be used which have a strong attraction for the leather, and hence go on well in the cold. If "acid" colours are employed, it is essential to select those which can be used in neutral solution, or at most with addition of some mild organic acid such as formic or acetic, since, as the leather is not washed after staining, the sulphuric acid would remain in it, and would ultimately destroy it. Where leathers have a hard and repellent surface the addition of a little methylated spirit to the dye is often very useful. The colours are used in solutions of from ¼ to 1 per cent., which should be quite clear and free from sediment. Difficultly soluble colours must be used in weak solution, or the dye kept warm while in use. Dye-solutions will not generally keep for any great length of time without change. Acid colours are sometimes employed dissolved in diluted "stearine glaze" (p. 494), and the use of sulphonated oil emulsions is worth trying.

Before staining, the leather must be carefully "set out," or otherwise made as smooth as possible, and the staining is generally done after most of the other operations of currying or dressing have been completed. Staining is best begun with the leather in a slightly damp or "sammed" condition, and the colour is applied evenly with a softish brush in two or three coats, the leather being slightly dried after each. As a rule, the more coats are applied the more even is the work; but to save cost of labour it is common on cheap goods to be content with two, of which the first is given, preferably with a weaker solution, to the dry leather. Where the leather is "weak-grained" it is sometimes advantageous to size it first with a weak solution of gelatine, gum tragacanth, or linseed mucilage, and similar solutions are often used to fix the colour and give a higher gloss. A weak solution of the stearine glaze mentioned on p. 494 is sometimes employed as a vehicle for the acid colours. Acid yellows and browns may also be dissolved in the undiluted glaze where only a pale colour is required, or to heighten the colour of leather already stained. A list of suitable colours for staining is given in Appendix C, p. 640.

It rarely happens in leather dyeing that the required colour can be given by the application of a single dye, most of the shades now required being produced by mixtures. It is, therefore, necessary to say a few words on the theory of colour combinations.

White light is of course composed of a mixture of all the spectrum colours, and can be separated into them by the prism. It is probable, however, that the eye is only capable of three distinct colour-sensations, and that all the colours we perceive are represented by the excitement of these in different proportions, the actual colour-sensations being red, blue-green, and violet.[1] If we interpose a piece of yellow glass between the eye and white light the violet and blue are absorbed, and the remaining red and green rays combine to produce the sensation of yellow. If

[1] The subject of colour is too complicated to be adequately treated here, and for fuller information readers are referred to Abney's *Colour Measurement and Mixture*, S.P.C.K., London, 1891. This is now, unfortunately, out of print, but there are several more recent books, among which may be mentioned Luckiesh, Constable, 1915. It may, however, be pointed out that, while the true primary colour-sensations are unquestionably red, blue-green, and violet, and by mixture of *light* of these colours all other colours, including white, can be produced, the primary *pigments* or *dyes* are red, yellow, and blue, the effect being produced in the former case by the addition of colours, and in the latter by their subtraction. Much useful information can be obtained by the use of a pocket spectroscope, or even of an ordinary prism fitted into a box (*e.g.* a cigar-box) with a narrow cardboard "slit" parallel with the prism at the opposite end. Dyed materials are examined in a good daylight, dye-solutions in test-tubes by daylight or in front of a Welsbach or electric light. The stronger the light the narrower the slit which should be used.

pure blue glass is used the red is absorbed, and we have blue as the result of the remaining mixture of green, blue, and violet. Red glass absorbs the whole of the green and greenish-blue, allowing red, yellow and much of the violet to pass. Thus if we combine blue and yellow glass only the green is allowed to pass, and similarly with red and blue glass green and blue is cut out, and only the violet remains. Thus red, yellow, and blue are frequently called the primary colours, and by combining all three in equal proportions all colours are cut out, and black or grey results. The blue and violet which are stopped by yellow glass are those colours which would produce the sensation of violet-blue, and hence the latter is called the " complementary colour " of yellow, and so on with the rest. It will be noted that all the colours of coloured objects are produced by absorption of a part of the light, and therefore coloured bodies are always darker than white ones, and where a colour is mixed with its complementary in suitable proportion, all colours are absorbed and black or grey is produced.

Colours which are made by mixing two primary colours are generally called " secondary " ; while the duller tints made by the addition to these of black, or of a complementary colour which produces black, are called " tertiary." Any primary colour is complementary to the secondary colour produced by mixing the other two primaries, and *vice versa*. The following tabular arrangement shows at once the effect of colour mixing:—

PRIMARY.	SECONDARY.		TERTIARY.
Red	Orange	with Black	Brown.
Yellow	Green	,,	Olive, Sage.
Blue	Purple (Violet)	,,	Puce, Maroon.
Red			

Theoretically, *any* colour may be obtained by mixture of the primaries, and that this is possible to a great extent is shown in the success of modern " three-colour " printing, by which pictures are obtained in natural colours by the use of three primaries only ; but in practice few colours are quite pure, and if two very different colours are mixed, it is difficult to avoid the production of tertiaries. The most brilliant colours are generally produced by dyeing with the nearest colour which can be obtained to that required, and shading with another which is near, but on the other side of the desired tint.

Thus if we want to produce bright shades in dyeing we must avoid the introduction of complementary colours. A bluish-red mixed with a reddish-blue will produce a bright shade of violet, but if we mix an orange-red with a greenish-blue we introduce yellow into the mixture, and obtain a dull maroon or puce, according to the proportion of the other colours. In a similar way, the introduction of a blue dye will dull a bright orange to a brown, and a little of a yellow dye will dull a bright purple to a maroon. This fact is frequently used in producing the quiet shades of colour often required from the most brilliant dyes. If to a bright orange we add black, or a blue dye which as its complementary produces black, we convert it into a brown. If instead of blue we use green for dulling we give the brown a yellower shade, since the green produces black at the expense of the *red* of the orange. Violet similarly used gives a redder brown, since it produces black by combination with the *yellow*. This shading, if small in amount, is frequently done by direct mixture of a suitable dye, but if considerable, it is generally better to top one colour with another. Thus a blue topped with a powerful orange will produce a Havanna brown. For dark colours it is frequently convenient to produce a dark ground with some cheap dye, such as logwood and iron or chrome, and to top it with a bright shade of the colour required. In this way cheap dark blues and greens can be easily produced. For reds and browns, mixtures of logwood and Brazil-wood, or Brazil-wood and fustic, may be used, topped with coal-tar colours. Tanning materials, such as quebracho and mangrove extracts, which give browns with bichromate, are also employed on cheap goods. It is also frequently wise to dye with a basic colour and top with an acid one, or *vice versa*, as in many cases the one fixes and combines with the other, and an increase of fastness is obtained.

Morocco and many other coloured leathers are finished by damping the surface of the dried leather with a very dilute "seasoning" of water, milk, and blood or albumen, allowing the leather to become quite or nearly dry, and polishing by friction under a cylinder of agate,[1] glass, or wood in the glazing machine. Many leathers are also grained by printing from engraved or electrotype rollers, or by "boarding," or a combination of the two. "Boarding" consists in pushing forward a fold in the leather on a table with a flat board roughed underneath, or lined with cork, in a way which is difficult to describe, but which in skilful hands wrinkles or "grains" the skin in a regular pattern.

The colour of a dyed skin is much altered by finishing, and

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[1] Agate is best for a final glaze, but hard wood (box or lignum vitæ) gets better to the bottom of the grain. Glass is less apt to "seize" in the machine if its high polish is taken off by fine emery or carborundum paper.

especially by glazing, which always darkens and enriches the colour. In dyeing to pattern it is useful to glaze a little bit of the rapidly dried skin by friction with a smooth piece of hard wood or bone (*e.g.* the handle of a tooth-brush) for comparison, and a portion of the pattern may also be wetted for comparison with the wet skin. Colours which look full and even in the dye-bath often go down in a most disappointing manner on drying, though to some extent they regain intensity on finishing.

In comparing the dyeing value of colours, the most practical way is to make actual dyeing trials with equal or known quantities of the colours and of water. Such trials may be made, either by " turning " the samples in photographic porcelain trays, kept warm in a water-bath (a " dripping tin " may be used for the purpose, the trays being supported a little above the bottom on tin supports soldered to the tin), or the leather may be hung from glass rods, by hooks of copper wire, in glass vessels (square battery jars), also placed in a water-bath. The leather samples should be of equal *surface* in every case ; for suspension, pieces of " skiver " (sheep-grain) of 8 by 4 inches or 20 by 10 cm. are very convenient. These may either be " pleated " or suspended by the two ends grain side out, with a short glass rod to weight the fold and keep them flat. The weight of colour used for a sample 8 inches by 4 inches multiplied by 54 times the area of a single skin in feet will give approximately the weight of colour needed per dozen, which is, however, a good deal influenced by the mode of dyeing and the quantity of water used.

In dyeing on the large scale, iron, zinc, and even copper are to be avoided, the latter acting very injuriously on many colours, and on the whole wooden vessels are to be preferred. Though these become deeply dyed, they become very hard, and if well washed with hot water, and occasionally with dilute acid, they may be cleansed so as to give up no colour in subsequent dyeing operations, though of course it is not desirable, if it can be avoided, to use the same vessel for very different colours. Probably slate, jointed with red lead or pitch, is the ideal material for dye-vats and paddles.

It is useless in the present state of the dye-trade to repeat former lists of leather-dyeing colours, but Mr M. C. Lamb has kindly furnished in Appendix C a list of the best colours now available, which of course must be considered as somewhat temporary, and which will probably be considerably extended in the near future. Zinc rapidly bleaches many colours, especially while wet and slightly acid, and discharge-patterns may often be produced by pressing the wet leather on perforated zinc plates.

CHAPTER XXIX

EVAPORATION, HEATING, AND DRYING

Questions of evaporation, whether for raising steam or for the concentration of tanning extracts and other solutions, are of considerable importance in the tanning industry, and as the same natural laws which apply to these equally govern the drying of leather, it is convenient to study the theory of the whole subject in one chapter, rather than to divide it and place each part in a different portion of the book.

The modern conception of evaporation and vapour pressures has been described on p. 86, but it will be necessary to recapitulate a little. It is a well-known fact that most liquids, if left exposed in an open vessel, gradually disappear by evaporation from the surface into the air, even at ordinary temperatures. If the vessel is heated sufficiently the liquid "boils," that is, bubbles of vapour are formed within it and escape, and the evaporation is therefore much more rapid. To avoid complication, let us first imagine a liquid sealed in a glass flask, which contains no air, but which is only partially filled by the liquid. It has been pointed out that the motion of heat by which the molecules of the liquid are agitated enables some of them to break away from the attraction by which liquid particles are held together and pass into the form of gas or vapour, which will fill the empty part of the flask. This evaporation will, however, soon reach a limit, since the vapour cannot escape from the flask. The flying molecules of vapour produce pressure by striking the walls of the flask, while a proportion of them will strike the surface of the liquid, and again be caught and retained by its attraction; and as the pressure rises, the number of these necessarily increases till a point is reached when as many fall back and are retained (or "condensed") as those which evaporate, and the pressure will then remain constant. The amount of the pressure will vary with the nature of the liquid, and will be the greater the more volatile it is, or, in other words, the less the power of its internal attraction. It will also increase with rising temperature, which, by increasing the velocity of motion of the molecules, renders their escape from the liquid easier, and their recapture more difficult. It will not be at all affected by the volume of vapour or the size of the flask, but so long as any liquid is present it will depend merely upon the nature of the liquid and the temperature. If the flask is large, more of the liquid will evaporate till the same pressure is reached. If at the outset the flask is not empty, but filled with air, it will make no difference to the pressure or quantity of the *vapour* in it, which will be *added* to that of the air, whatever that may be. If the sealing of the flask is broken so that it is open to the atmosphere air and vapour will escape, or air will pass in, till the total pressure is equal to the atmospheric pressure outside (about 15 lb. per square inch). As, however, the vapour in the flask is always renewed by evaporation, so that the full vapour-pressure of the liquid is maintained, the "partial" pressure (as it is called) of the *air* in the flask will be less than that of the outer atmosphere by the amount of the vapour-pressure, which makes up the difference. Once this balance is attained, evaporation will go on very slowly in the flask, as it can only replace the small quantity of vapour which escapes. If, however, the vapour is removed by blowing fresh air into the flask, it will rapidly be replaced in the old proportion by fresh evaporation. Thus goods in a close room will dry only very slowly, even if the temperature is high, unless the moistened air is replaced by drier air from the outside by some effective system of ventilation. In absence of this, evaporation only becomes rapid when the temperature of the liquid is raised to its "boiling point," that is, when the vapour-pressure becomes slightly in excess of that of the atmosphere, so that the freshly formed vapour can push out that already in the flask or chamber into the outer air, and at the same time bubbles can be formed in the interior of the liquid by the escaping vapour. As the vapour-pressure of a liquid rises continuously with increasing temperature, and its boiling point is defined as that temperature at which it is equal in pressure to the air (or vapour) in contact with it, it is evident that the boiling point must entirely depend on the pressure. Thus the boiling point of water in a boiler at a pressure of 55 lb. per square inch above the atmosphere is 150° C., and in a partial vacuum equal to 5·8 inches of barometric pressure is only 60° C., a fact which is made use of in the concentration of extracts and other liquids at a low temperature in the vacuum-pan and in the Nance system of tannings (p. 572). (Atmospheric pressure is taken at 30 inches or 760 millimeters of the barometer, or 14·7 lb. per inch, or 1·033 kilos per square centimeter.[1])

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[1] The German spelling of metrical units has been allowed to remain from the first edition, both to avoid extensive correction and because

If a piece of iron is placed over a powerful gas-burner it will go on getting hotter till its temperature is nearly or quite equal to that of the gas-flame. On the other hand, a pan of water, in the same condition, once it has reached its boiling point, becomes no hotter till all the water is evaporated. It is evident that the whole available heat or energy of the gas-flame is consumed in converting the water into steam. We might convert a proportion of this energy into mechanical work by using the steam in a steam engine; but even without this, work is actually being done by the escaping steam in raising the weight of the atmosphere, and in overcoming the attractive force which holds the particles of water together in the liquid form. It is of course known to everyone that though energy may change its form, as from heat to work, it cannot be destroyed, diminished, or increased; and therefore the whole of the work performed in converting the water into steam is again recovered as heat when the steam is condensed. In this connection a clear distinction must be made between *quantity* of heat and *temperature*, which in popular language are often confused. It is, for instance, obvious that if we mix a pound of water at boiling temperature with another pound at freezing point the temperature is altered to 50° C., but the total *quantity* of heat is unchanged. It is equally clear that no change in quantity of heat takes place when 1 lb. of mercury at 100° is mixed with 1 lb. of water at 0°, though in this case, owing to the small capacity of mercury for heat, the common temperature would only be raised to about 3°. We must therefore have some measure of quantity of heat apart from the mere direct indications of the thermometer, and that most generally used is the quantity of heat required to raise 1 kilo of water 10° C. (kilogram-calorie).[1] In England the heat required to raise 1 lb. of water 1° F. is also in use as a unit. The k.-calorie is equal to 3·97 (very approximately 4) lb. × F. or B.T.U.[2] For our purpose it may be taken that 100 k.-calories of heat are required to raise 1 kilo or litre of water from freezing to boiling

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it is phonetic English, and it seems unnecessary to adhere to a French spelling where we do not adopt the French pronunciation (*cp*. Appendix A).

[1] A gram-calorie of one-thousandth part of the above is also in use for some scientific purposes, but the kilogram-calorie only is used in the following pages.

[2] This unit, commonly known as the B.T.U., or British thermal unit, *i.e.* the quantity of heat required to raise 1 lb. of water 1° F., is much less convenient in calculation than the calorie, and it is a pity that it has been legalised as the unit of heating power by which gas must be sold, since it will involve an additional change when we adopt decimal weights and measures.

temperature. If, however, the water is actually frozen we require 80 k.-calories merely to melt the kilogram of ice without perceptibly raising its temperature, and when the water is raised to 100°, 536 calories of heat are still necessary merely to convert it into steam at the same temperature. To melt 1 lb. of ice requires 144 B.T.U.,[1] to raise it to boiling point 180 more, and to evaporate it 965 additional. The quantity of heat required for actual evaporation varies a little at different temperatures, being somewhat larger at lower temperatures, but the total heat required to raise water from the freezing point and convert it into steam at *any* pressure is nearly constant, being 635 calories at atmospheric pressure, and only about 650 calories, or 1180 B.T.U., at 50 lb. per square inch. The quantity of heat evolved by the combustion of 1 lb. of good coal is 13,000 to 15,000 B.T.U., or of 1 kilo, 7200 to 8300 k.-calories, but in raising steam in a good boiler, coal will only evaporate 10 times its weight of water at 100° (5360 calories or 9650 B.T.U.), the remaining heat being lost. One horse-power (33,000 foot-pounds per minute)[2] in the best engines requires about 1½ lb. of coal or 15 lb. of steam per hour, but in those of worse construction may run up to many times that amount. As, even theoretically, not 20 per cent. of the total heat can be converted into mechanical work in a "perfect" engine working at 75 lb. pressure, it is often economical to use waste steam for heating or evaporation, and where this can be done, the additional cost of the mechanical power is very small. The "internal combustion" (gas) engine is decidedly more economical in heat used, and the Diesel oil engine is still more so, since they work at much higher temperatures.

In evaporating liquids in the open pan 536 calories is required to evaporate 1 kilo of water already raised to boiling temperature, and a larger amount for salt-solutions, and it makes comparatively little difference whether this is done at 100° or at a higher or lower temperature. Where, however, evaporation is done *in vacuo* considerable economy can be effected by what are known as multiple "effects," in which the steam from one vacuum-pan is employed to boil a second under a reduced pressure, and consequently boiling at a lower temperature. This principle can be practically applied to as many as five or six successive "effects," the weaker liquor being usually evaporated at the

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[1] It might seem at first sight that as 1 k.-calorie=3·97 B.T.U., 317·6 of the latter would be needed to melt 1 lb. of ice, but it must be remembered that 1 lb. is only 0·456 kg., and multiplying by this we get 144.

[2] This is equal to 76·04 kilogrammeters per second, but the metrical horse-power is only taken at 75 kilogrammeters in France and Germany.

highest temperature and lowest vacuum in the first "effect" by the exhaust steam of the engine used for the vacuum pumps, while the steam from the first effect heats that of the next higher concentration, and so on. In the Yaryan evaporator (p. 408) the boiling liquid is sprayed through coil-tubes, thus exposing an enormous surface to evaporation, and the whole concentration of any given portion of liquid takes place as it passes through the apparatus, which does not, even in multiple effects, occupy more than four or five minutes, and without the temperature of the liquid ever rising above 60° or 70° C. In the case of liquids like sugar- and tannin-solutions, which are liable to chemical change from continued heating, the shortness of the time is a very great advantage. The number of effects which it is desirable to use depends greatly on the cost of fuel as compared to the largely increased cost of the apparatus. One lb. of coal employed in raising steam will evaporate 8½ lb. in a single-effect Yaryan, 16 lb. in a double-effect, 23½ lb. in a triple, 30½ lb. in a quadruple, and 37 lb. in a quintuple-effect apparatus,[1] but as a rule more than three or four effects are not advisable (see also p. 407).

Where liquids are evaporated in the open air at temperatures below boiling it is advisable by some means to spread the liquid in a thin film, so as to expose a large surface, which must be continuously removed by agitation so as to prevent the formation of a skin. An apparatus for this purpose is the Chenalier evaporator (fig. 110), which consists of steam-heated copper discs rotating in a trough containing the liquid, which is taken up by buckets attached to the rims of the discs and poured over their heated surfaces. In other forms the liquid is allowed to trickle over steam-heated pipes or corrugated plates. Such evaporators should be placed in a current of air so as to rapidly carry off the vapour formed. Their use is very objectionable for liquids like tannin-liquors, which are injured by oxidation, and they are not nearly so economical as vacuum-pans.

The drying of leather depends on the same laws as the evaporation of liquids, but demands special consideration from its very different conditions of temperature and supply of heat. It is important to remember that evaporation cannot go on unless the vapour-pressure of the liquid to be evaporated is higher than that of the vapour in contact with it, and that air-pressure

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[1] Of course a similar economy without vacuum may be effected with solutions not injured by temperature by working the first "effect" at high pressure and temperature and coming down through successive effects to boiling point and atmospheric pressure, though this is not so commonly done.

does not prevent evaporation, so that if we sweep away the stagnant vapour with dry air, evaporation will go on as quickly as *in vacuo*, except that the liquid cannot boil. We must also bear in mind that evaporation consumes quite as much heat at low temperatures as in a steam boiler, and that this heat must generally come from the surrounding air, the temperature of which it reduces.

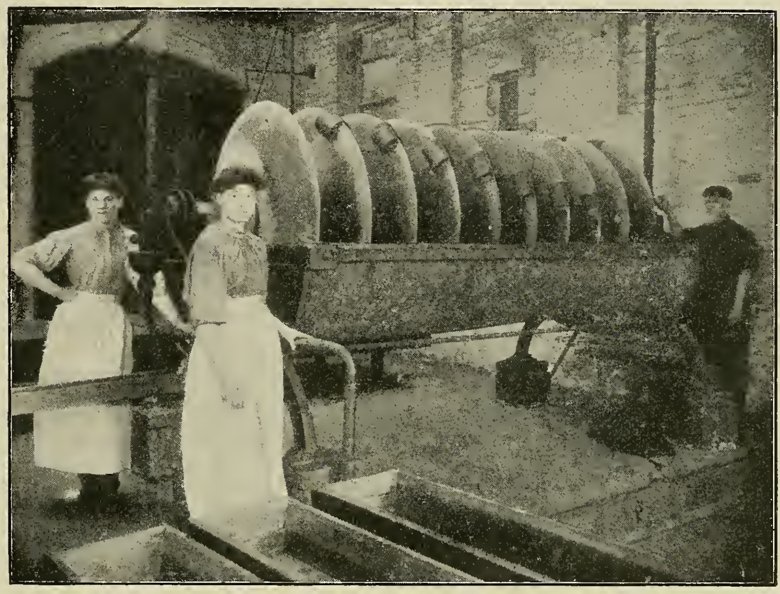

FIG. 110.—Chenalier Evaporator and Glue Coolers.

The rapidity of evaporation, and the quantity of moisture which can be taken up by a given volume of air, depends on the vapour-pressure, which increases with temperature. The relation between the two, and the weight of water in grams per cubic meter which can be dissolved in dry air, is given in the following table. (Grams per cubic meter is practically equivalent to ounces per 1000 cubic feet. Vapour-pressure is given in millimeters of mercury of the barometer, p. 513.) 100 mm.=3·94 inches.

VAPOUR PRESSURE OF WATER

Temperature, °C.	−10	−5	0	5	10	15	20	25	30	35	40
,, °F.	14	23	32	41	50	59	68	77	86	95	104
Pressure, mm.	2·2	3·2	4·6	6·5	9·1	12·7	17·4	23·5	31·5	41·9	54·9
Grams per cub. m.	2·4	3·4	4·9	6·8	9·3	12·8	17·2	22·8	30·1	39·2	..

Air is practically never dry, and in damp weather is frequently saturated with moisture to the full extent corresponding to its temperature. In England the average quantity of moisture contained in the air throughout the year is 82 per cent. of the total possible, and even in the driest summer weather it is never less than 58 per cent. So long as the water is in the form of vapour the air remains quite clear and does not feel damp; in fogs the air is not only saturated with moisture, but contains small liquid particles floating in it.[1] Of course when the air is really saturated with moisture it has no drying power whatever.

As is evident from the table, the amount of water which can be dissolved in a given volume of air rapidly increases with temperature. Air at 0° C. is only capable of containing 4·9 grams per cubic meter, or not much more than 20 per cent. of what it can contain at 25° C. It hence rapidly increases in drying power as it is warmed, and consequently the air in a warm well-ventilated drying room in winter is generally much drier, and has greater capacity for absorbing moisture than the open air in the driest summer weather. This is the principal cause of the tendency to harsh and irregular drying by the use of artificial heat, and may be remedied by a proper circulation of the air by a fan without too frequent change with the colder air outside. On the other hand, the use of a little artificial heat in damp summer weather, when the air is saturated with moisture, may be quite as necessary as in winter. The amount of moisture in the air is most easily ascertained by a device known as the "wet and dry bulb thermometers." This consists of two thermometers mounted on a board, one of which has the bulb covered with muslin, and kept moist by a lamp-wick attached to it and dipping in a vessel of water. The temperature of the wet bulb is lowered by the heat consumed in evaporation, and the difference of its temperature from that of the dry bulb is proportionate to the drying power of the air. This may be approximately calculated in grams per cubic meter by multiplying the difference by 0·64 for Centigrade or 0·35 for Fahrenheit degrees, and if deducted from the total capacity for moisture corresponding to the temperature of the *wet* bulb as given in table, p. 517, will give the actual moisture in grams contained in a cubic meter of air; but for practical purposes, all that is necessary is to find by experience the temperature and difference between the wet and

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[1] The reason that a fog feels so much colder than its thermometer-temperature is, that in warming it to body-temperature we have to expend the latent heat required to convert these liquid particles into vapour, and in a frost-fog also to melt the ice.

dry bulbs which gives the best result for the drying required, and to maintain it as nearly as possible by regulation of the heating and ventilation. Cheap forms of the instrument are made for use in cotton-mills, where it is necessary to maintain a certain degree of moisture ; or it may be improvised from two chemical thermometers which agree well together. Distilled (rain or steam) water should be used to moisten the bulb, or it will quickly become coated with lime salts, and it should be placed in a moderate draught, or its indications will not be accurate.

It is of course obvious that not only the wet thermometer but the wet hides or skins are cooled by evaporation, and they, in their turn, cool the air with which they are in contact, which not only becomes moistened, but is lessened in its capacity for moisture by cooling, and thus rapidly reaches a condition when it can absorb no more moisture. It is thus necessary to maintain its temperature by artificial heat, or to replace it constantly by fresh air from the outside, and which of these expedients is most economical will depend on the temperature of the air outside as compared with that which it is required to maintain. If the outside air is sufficiently warm, and not saturated with moisture, it is generally best to use it in large quantities without artificial heat, wind usually supplying the necessary motive power for its circulation.[1] Wet goods from the pits may thus be dried to a "sammed" condition by any air which is not saturated and is above freezing point, though the drying will often be slow. For drying "off," artificial heat is usually necessary, since the attraction of the fibre for the last traces of moisture is very considerable, and to remove it the drying power of the air must be considerably higher than that required for the evaporation of free water.[2] In drying stuffed leather a temperature must generally be maintained sufficient to keep the fats employed in partial fusion, and so permit their absorption by the leather, while at the same time the drying must be gradual, or the water

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[1] Compare also p. 553 on construction of tanneries.

[2] Commercially-dry leather generally, if unstuffed, contains about 15 per cent. of residual moisture, which varies in amount with the weather, and can be more or less completely removed by drying at high temperatures. If leather has been over-dried, it only slowly regains its weight on exposure to cold air. Commercial disputes not unfrequently arise on the dryness of leather. In the opinion of the writer, a customer can only claim that the leather should be sufficiently dry not to lose weight when exposed to dry air at the ordinary temperature and degree of dryness of a warehouse or factory, and claims based on re-drying in hot drying rooms are distinctly fraudulent.

may be dried out before the fats have time to take its place. This is generally best attained by the use of artificial heat, and ventilation by circulating the air by a fan without its too frequent renewal, especially in cold weather. Frequently air which has been heated and used for drying off finished goods, and so partially saturated with moisture, may be used with advantage for wet goods, or for other purposes where a more gentle drying is required. If the temperature is low outside, the amount of heat consumed in heating cold air to the temperature required may be very considerable. The weight of a cubic meter of air at 0° C. and atmospheric pressure is 1·293 kilos, and its specific heat at constant pressure is 0·2375 of that of water. Therefore to heat a cubic meter of air at ordinary pressure and temperature 1° C. will require the same amount of heat as that used to heat 0·307 kilo of water to the same extent, or in other words 0·307 of a k.-calorie.[1] If steam-heating is used, 1 kilo of good coal burnt under the boiler should heat about 1800 cubic meters 10° C., or 1 lb. should heat 52,000 cubic feet 10° F., assuming that the condensed water is not cooled below 100° C. These seem large volumes, but if we reflect that a 48-inch Blackman fan may move 30,000 cubic feet per minute, we shall realise that the cost of coal in heating air is not inconsiderable.

We must now consider the heat consumed by the actual evaporation of the water in the leather. The actual evaporation of water already raised to 100° C. consumes 536 k.-calories, but the evaporation of water which has not previously been heated so far consumes more heat, and we may take that required at ordinary temperatures as in round numbers 600 k.-calories per kilo, or 1080 B.T.U. per lb. Disregarding small fractions, this is equivalent to the cooling to the same temperature of an equal weight of steam in the heating pipes, and this, as we have seen, demands about $\frac{1}{10}$ of its weight of coal for its production from water already heated to 100° C.

The cooling takes place, in the first instance, in the leather, the temperature of which is reduced like that of the wet-bulb thermometer, and this in its turn cools the air in contact with it. Thus in air-drying without artificial heat the whole heat must be supplied by the air, and the loss reduces its capacity for

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[1] For those who prefer English measures, a room of 10 feet cube or 1000 cubic feet or 28·12 cubic meters contains 80·43 of air at freezing point and mean barometer pressure, and requires 19 B.T.U. to raise the temperature 1° F., or 8·6 calories to raise it 1° C. As the temperature rises the weight of air becomes less, and takes somewhat less heat to raise it 1°. At 65° F. only about 18 B.T.U. is required.

moisture, greatly increasing the volume required. This is not of much consequence in open-air drying, since even a light wind will supply air in enormous volume. A moderate breeze of ten miles an hour moves about 15 feet or $4\frac{3}{4}$ meters per second. When, however, the air must be moved by fans, the power required becomes important. The evaporation of 1 kilo of water at summer temperature will cool about 2000 cubic meters, and that of 1 lb. 32,000 cubic feet of air 1° C.

In calculating the ventilating and heating power required in fitting up drying rooms it is usually necessary to ascertain that required under the most unfavourable circumstances, and then add a liberal margin to cover errors and accidents. As the calculations are, in consequence of the many varying conditions, somewhat complex, it may be convenient to give as examples the quantities of air and heat required to evaporate 1 kilo (2·205 lb.) of water under different ordinary conditions, and these may serve as a basis of calculation of the drying power which must be provided for different tanneries.

1. *Indifferent Open-air Drying.*—Air at 10° C. (50° F.), wet-bulb thermometer 7° C. (44·3° F.), indicating a total capacity for moisture of about 2 grm. per cubic meter; air not to be cooled beyond 7·75° C. (46° F.), leaving a residual capacity for moisture of 0·5 grm. per cubic meter. Each cubic meter will therefore take up 1·5 grm. of moisture, and as 1 kilo contains 1000 grm., we have

$\frac{1000}{1\cdot5}=666$ cubic meters per kilo required to absorb moisture;

and $\frac{600}{2\cdot25^\circ\times0\cdot3}=888$ cubic meters reduced 2·25° to furnish the 600 calories required for evaporation. Total air used 1554 cubic meters or 54,900 cubic feet.[1]

2. *Drying with Heat.*—Outside-air at 10° saturated with moisture heated to 20° C. (68° F.) acquires a capacity for 7·9 grm. per cubic meter. If we assume that a drying capacity of 2 grm. per meter is required to complete the drying, we have an effective capacity of 5·9 grm.

$\frac{1000}{5\cdot9}=170$ cubic meters or 6000 cubic feet, and to heat this 10° C. will require 510 calories. Evaporation of 1 kilo will consume 600 calories. Total heat 1110 calories.

3. *Drying with Heat.*—Outside-air at 10° as above heated to 25° C. giving an effective capacity for moisture of 13·5 to 2·0=11·5 grm. per cubic meter.

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[1] 1000 feet^3=28·314 m.^{3}, or 1 m.^{3}=35·310 feet^3.

$\frac{1000}{11 \cdot 5} = 87$ cubic meters or 3070 cubic feet. To warm this 15° requires 391 calories, and 600 calories added for evaporation gives a total of 991 calories.

Comparing 2 and 3 we see that the higher temperature is more economical, where it can be allowed, than the lower, both in air and heat, though this is partly compensated by the greater loss of heat by cooling of the building, etc., which it entails.

4. Air at 0° C. heated to 20° requires about 97 cubic meters or 3430 cubic feet of air, and a total of 1180 calories.

5. Air at 0° C. and heated to 25° C. requires 63 cubic meters or 2230 cubic feet, and a total of 1075 calories.

6. Air at −15° C. (5° F.) requires 4·5 calories per cubic meter to raise it to 0° C., and acquires a capacity for drying of about 2 grm. per meter.

We will apply these figures to a drying room arranged with a screw-fan with a central division, or two floors, so that the air can be either circulated or replaced with fresh air from the outside at will (see fig. 112). Such a room with 100 feet of length clear of space required for fans, air passages, and heating pipes, and 20 feet by 8 feet in section, should hang about 800 medium butts, weighing say 12½ kilos (27 lb.) each, and when wet from the yard containing the same weight of water. A 48-inch Blackman fan under these conditions would probably move say 20,000 cubic feet (565 cubic meters) of air per minute at the cost of 2 or 2½ horse-power. This, in a room of the section named, would give an average velocity of 125 feet per minute or rather under 1½ miles an hour; not at all too much to keep the air freely circulating among closely hung leather. If we assume that these butts are to be dried in a week (practically 10,000 minutes) under the conditions of No. 2, the 10,000 kilos of water they contain will require 1,700,000 cubic meters of air, or about 170 cubic meters per minute, or about $\frac{3}{10}$ of the air must be fresh every time it passes through the fan. One kilo of water requiring 1110 calories must be evaporated per minute.

Under the conditions of No. 4 only 97 cubic meters of air per minute would be required, or about $\frac{5}{6}$ might be circulated without change, but the total heat required would be about the same, 1180 calories. Under the conditions of Nos. 5 and 6 some 1620 calories per minute would be employed. It is hardly necessary to provide for the full amount of heat required by No. 6, since in this country such conditions occur but seldom, and never for more than a few days at a time, and during such a period much less heat would suffice to carry on the drying at a slower rate and keep out the frost.

Beside the heat required for actual drying it is necessary to provide for that lost by the building during cold weather, and this is much more difficult to calculate. If, by arranging the outlet for moist air on the pressure side of the fan, the internal pressure of the building be kept a little lower than the outside there can be no loss by escape of hot air, any leakage being inwards, and supplying a part of the change of air which, we have seen, is necessary. In a brick building with glass windows the loss of heat is far less than in the old-fashioned wooden louvre-boarded structure, and where fan-drying is in constant use the brick structure is much to be preferred. Frequent windows, with casements horizontally pivoted at the centre, will supply enough air for favourable conditions of air-drying, and when the weather is bad, resort is had to the fan. Most modern drying rooms in the Leeds district are built upon this plan. Where louvre-boarded structures must be used for fan-drying the sides should be made as tight as possible in winter by sheets of canvas or sail-cloth nailed on, for which purpose old sails can be bought in seaport towns at reasonable rates, a few louvre-boards only being kept open for the admission of air in suitable positions.

Box, in his *Practical Treatise on Heat*,[1] puts the loss through walls in brick buildings for a difference of 30° F. (16·6° C.) between inside and outside temperatures at the approximate amounts shown in the following table:—

Loss of Heat through Walls

Thickness of Wall in Inches.	K.-calories per Sq. Foot per Hour.	
4·5	1·76	Stone walls must be about one-half thicker, to afford equal warmth with brick ones.
9	1·44	
14	1·20	The loss from glass windows amounts to 3 or 4 k.-calories per square foot per hour.
18	1·06	

If walls are built with an air-space, as is now common, the loss of heat would be lessened.

If the building is of several stories, the loss to the roof in the intermediate ones need hardly be taken into account; but if the ceiling is not tight, and open to the roof, the loss may be great,

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[1] E. & F. N. Spon, Ltd., London.

but difficult to estimate. If we consider the drying room already described, the total area of the walls and ceiling is about 4000 feet, and to maintain its temperature 30° F. above the atmosphere at 1·2 calories per square foot would require 4800 calories per hour or 80 calories per minute, a very small amount compared to that consumed in drying.

The following table calculated from data given by Box will give some idea of the amount of steam or hot-water piping required for heating. The sizes given are for the internal diameter of the pipe, allowance being made for the increased heating surface of pipes of ordinary thickness. Small pipes are considerably more effective in proportion to their surface than large ones, and for high-pressure heating 1½ or 2-inch wrought-iron pipes are to be recommended as in many ways preferable to cast iron. The gilled or ribbed pipes now often used are also advantageous as giving a greatly increased heating surface.

The temperature of the air to be heated is understood to be 60° F.; at lower temperatures the quantity of heat given off by the pipes would be greater, and at higher temperatures less, the amount being approximately proportional to the difference of temperature between the air and the hot pipes. It is also important to note that the table refers to steam-pipes in still air, and that if placed in a powerful draught (as immediately before or behind the fan) their heating effect may be at least doubled. This has not been considered in the following calculations.

HEAT GIVEN BY STEAM-PIPES

Steam Pressure, lb. per sq. in.	Temperature of Pipe.		K.-calories per hour per foot run of Pipe.		
	°C.	°F.	2 in.	3 in.	4 in.
52	149	300	102	137	169
35	138	280	92	121	148
21	127	260	81	106	130
10	116	240	68	92	113
2·5	104	220	59	81	97
	99	210	54	72	89
	93	200	49	66	81
	88	190	45	60	74
	82	180	40	54	67
	77	170	36	49	60

Applying these figures to the estimate of 1110 calories per minute required for drying in our building, and assuming 80 calories per minute for the loss of heat through the walls, we have a total of about 71,400 calories per hour, and to obtain this would require 736 feet of 4-inch pipe at 220° F. (heated by exhaust steam), or 700 feet of 2-inch pipe heated to 300° F. by steam at 52 lb. pressure.

If we adopt the estimate of 1620 calories of Nos. 5 and 6 we shall require 1050 and 1000 feet of the two pipes respectively, and this covers approximately the worst conditions. We must, however, remember that these estimates are made for continuous drying during the twenty-four hours, and that if the fan and steam are only applied during a portion of this time the supply both of air and steam must be proportionately increased, or the time of drying correspondingly lengthened.

It is very desirable, however, that the fan should be driven by a small separate engine, the steam for which will only form a small proportion of that required for heating, and of which the whole of the heat will be recovered, since even that utilised in driving the fan will again be converted into heat by the friction of the air, and will therefore cost nothing. This arrangement will enable the drying to proceed so long as the necessary steam is maintained, which in bad weather can easily be done by the night watchman. It may also be pointed out that, during a great part of the year, the goods can be dried to a "sammed" condition without heat or in the open air, or in the case of dressing leather a considerable part of the water can be removed by pressing or squeezing, effecting a further economy.

It must be left to the reader to apply the same calculation to other sorts of leather than sole, but it may be pointed out that the essential point, as regards heating and ventilation, is the weight of water to be evaporated in a given time, and that the actual size and shape of the drying room is unimportant so long as adequate heating and circulation of the air between the leather is secured; and these remarks also apply to the particular form of fan or other ventilation employed, and to the means of heating. As the quantity of heat consumed is very considerable, it is well to look out for sources of waste heat which can be employed, or for means by which the heat of the fuel can be more directly and completely utilised than it is in raising steam. Thus a large amount of heat can sometimes be obtained by passing air through pipes or "economisers" fitted in a chimney-flue;[1] or gilled stoves or "calorifers" may be used in a separate chamber to directly heat the air which is drawn in by the fan.

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[1] These pipes should be provided with scrapers to remove soot, as in Green's economiser, or their efficiency will be much diminished.

Figs. 111 and 112, furnished by the James Keith and Blackman Co. Ltd., give a good idea of the construction of screw-fans, of which there are now many different patterns, and the general principle of arrangement of fan-drying rooms, the air in this case being circulated in opposite directions on two floors, and the amount of change being regulated by the shutters at A, etc. The grouping of pipes at the ends of the two floors which it shows is in general a good arrangement, but the length between them should not be too great, or the drying will be unequal in different parts of the room. Sometimes this is convenient ; thus if most of the heat be supplied to the air coming fresh from the inlet of the upper floor, the damper and colder air of the lower room can be continuously used for drying wet goods from the yard, and the upper reserved for drying off the finished leather. A disadvantage of this plan is that open-air drying can seldom be utilised except in an elevated building ; and even when it is adopted, means should be provided for heating the lower room in cold weather. In place of two floors it is obvious that a single floor may be divided into two compartments by a longitudinal partition. Whatever pipes are grouped at the ends of the building, it is advisable to arrange sufficient to prevent frost, against the walls, or in the old-fashioned way on the floors

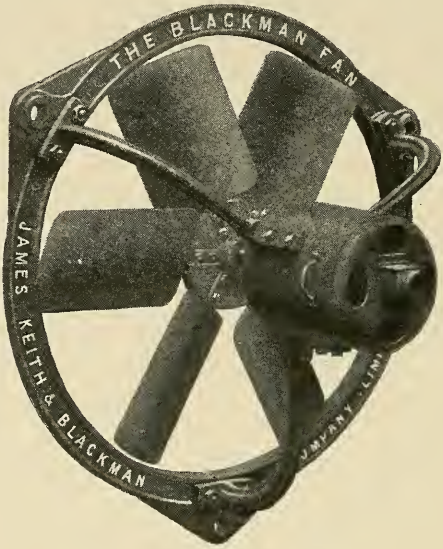

Fig. 111.—Blackman Fan.

beneath the leather, but not too close to it, and protected by a wooden lattice on which the workmen can stand, which also

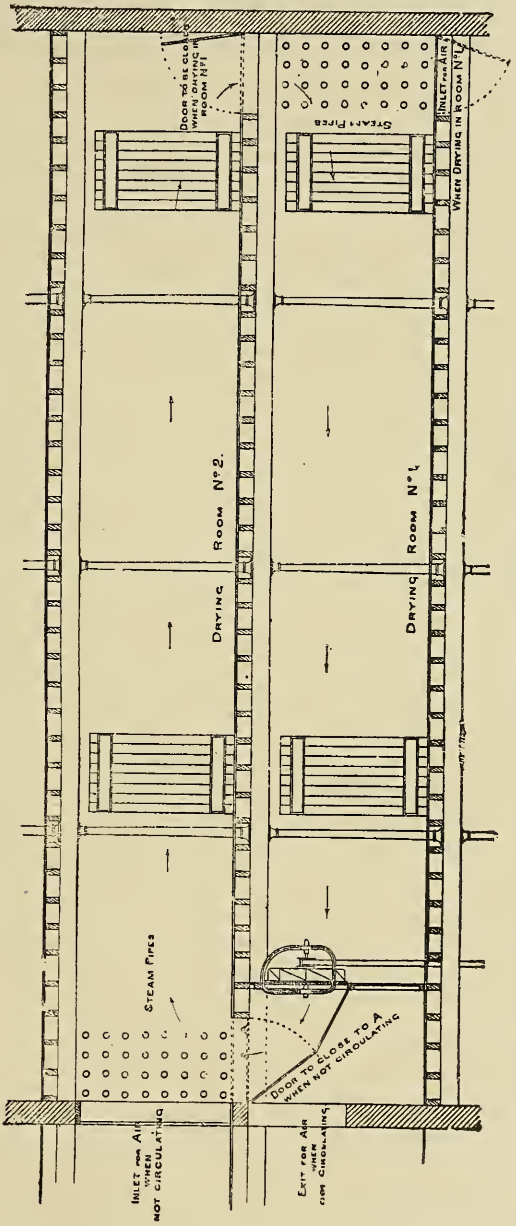

FIG. 112.—Section of Drying Rooms with Fan.

removes the risk of accident from wet leather falling on the hot pipes. The latticed space should be open at the end facing the air current so as to receive a portion of the draught, which will become heated and ascend, its place being taken by damp and cold air from the leather to be re-warmed. Water-vapour in itself is lighter than air, but the contraction produced by the cooling of evaporation more than compensates this, and the damp air is therefore heavier than the dry. The arrangement of hot pipes near the ceiling of a drying room, which has been borrowed from some American tanneries, is wrong in principle, unless the air is forced in at the upper part of the room or the upper floor is latticed, and only acts in other cases when the air is thoroughly mixed and circulated by mechanical ventilators; while pipes near the floor will continue to produce a certain amount of circulation of the air, even when the fan is not running. In protecting pipes by lattices care should be taken not to confine them too closely, or their heating effect will be seriously diminished. In fan-drying, leather is preferably hung edgeways to the current of air, so as to allow of its free and uniform passage between. In the case of sole leather the butts or bends are conveniently suspended by **S**-hooks of brass or iron wire to hooks or nails fixed in the joists. If gangways between the leather must be left in the direction of the draught, they should be closed at intervals in the length of the room by curtains or shutters, so as to deflect the air-current into the leather.

Screw-fans like the Blackman can be used either to suck or to blow the air, though the former is preferable where it can be arranged, because it produces a more uniform current in the room. On the blowing side the air issues with considerable velocity in a sort of cone, but little coming through the centre of the fan, while that near the edges spreads rapidly from its centrifugal motion. This is rather advantageous where the fan blows into an open room, but involves waste of power where it discharges into narrow and square airways. The ends of the vanes of the Blackman may be turned in at the rim of the fan to prevent this tangential discharge, but it is probable that where a fan is to *blow* into a room it would be more advantageous to put it on the inner side of the wall, and without curved ends to the vanes, so as to distribute the air as widely as possible. A somewhat similar result would be attained with a Blackman by placing it in a position the reverse of that for which it is intended, and running it also the reverse way, but its " efficiency " might possibly be lessened.

Screw-fans are good for moving large volumes of air at comparatively low velocities and against little or no resistance, but they are quite unsuitable for forcing air against high resistance or through narrow channels, and for this purpose centrifugal fans like the Capel (fig. 113) are much more suitable, and mechanically more efficient. In any case there is much loss of power in forcing air through narrow airways, and if a screw-fan must be employed for the purpose, the channel should be as large in section as the area of the fan, and all sharp angles in its course should be avoided. There is great loss of power where a current of air or water has to pass suddenly either from a wider to a narrower channel, or the reverse, and in both cases the resistance is diminished by making the enlargement or contraction gradual or "bell-mouthed." Thus a pipe conveying water at a given head

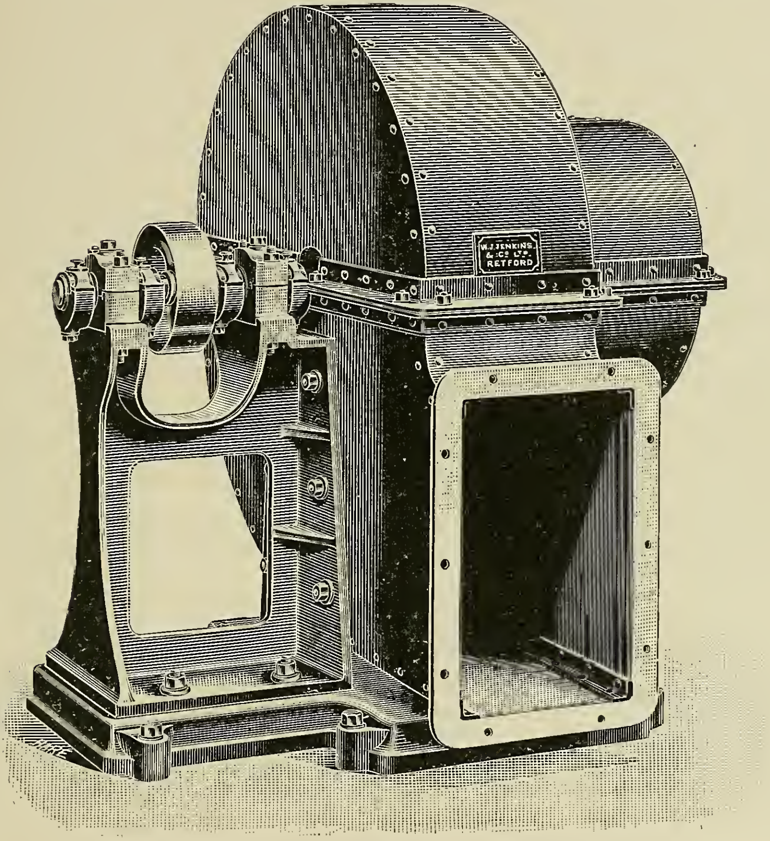

FIG. 113.—Capel Centrifugal Fan.

into or out of a cistern will discharge a much larger quantity if the ends are bell-mouthed than if it terminates abruptly. For the same reasons, air suffers considerable resistance if it has to pass suddenly into or out of a larger space, such as a drying room, and unnecessary partitions and other abrupt changes of dimension in the current should be avoided. Curves should also take the place of angles as much as possible.

Systems in which air is drawn or forced over systems of heating pipes by a centrifugal fan, and then distributed through comparatively small airways among the leather which is to be dried, are in some cases convenient and advantageous. Among these may be mentioned the Sturtevant and the Seagrave-Bevington. There can be no valid patent on the general principle of heating by distributing air in this way, but only on the particular arrangement or appliances used in the special case. Centrifugal fans should be considerably larger in diameter than in axial length, those with long vanes of small radius being wasteful in power from the insufficient supply of air to the centre. There is also no reason why, in some cases, centrifugal fans should not be substituted for screw-fans in drying on the system which I first described, especially in cases where the air has to encounter considerable resistance, as, for instance, in traversing a filter to remove dust. One of the best filters for this purpose is a table of wire-gauze or fine netting covered to a depth of 3 or 4 inches with loose wool. Hair or cheaper fibrous materials may be substituted for the wool, but are less efficient. The air must of course be sucked downwards through the gauze. When the wool becomes dirty it may be washed, if possible in a wool- or hair-washing machine, and again spread on the table in a damp condition, as it will quickly be dried by the current of air. Flannel is also useful where the wool-filter is impracticable, but requires frequent washing.

Apart from wind, natural ventilation is seldom to be relied on for drying on any considerable scale. Heated air is, of course, lighter than cold, and this is the cause of chimney-draught, but to get a good circulation in this way a high shaft and high temperature is required. Nevertheless, in one of its best forms the method has been a good deal used in America in the so-called "turret-dryer," a building of seven or eight stories in height, constructed of wood with latticed floors, and heated by steam-piping at the bottom, where the air is admitted. The method is not likely to be much used in this country, as, apart from the questions of cost of building, fire risk, and trouble of raising and lowering the leather, a good draught will only be obtained when the outer temperature is low in comparison to that inside, and in our milder and moister climate the conditions are not nearly so favourable as in the United States. As the air is rendered heavier by the cooling of evaporation to a larger extent than it is lightened by the water vapour there is a tendency in drying by upward ventilation for the warm air to form local upward currents, while the cold and damp air falls back, and from this irregularity of flow it is difficult to saturate the air equally. This may be avoided by downward ventilation, in which the warm air is admitted at the top of the drying room, and the cold and damp air allowed to escape at the bottom. This fact suggests that in using systems of drying, such as the Sturtevant, it would be better to place the distributing pipes at the top rather than the bottom of the room, but in this case care would have to be taken that there were no openings left by which the air could escape at the top of the room without descending through the leather. If this be avoided, the warm air will float on the top of the colder and damper and press it uniformly down and out. I believe the merit of first having applied the principle of downward ventilation to leather-drying is due to Edward Wilson of Exeter. It is necessary that the hot air should be *forced* in at the top, or the cold air *sucked out* from the bottom ; and the mere placing of hot pipes near the top of the room (p. 528) will not cause the required circulation. Wilson placed his heating pipes in a partitioned space at the side of the room, at the bottom of which cold air was admitted from the outside, which escaped into the room at the top. As the temperature of this side chamber was high and the air consequently light an upward current was produced in it, though probably somewhat inefficiently, as the height of the column of heated air could only be small. Assisted by a fan, and circulating a part of the air, the method should give good results, especially over two (latticed) floors. As the air could not be satisfactorily heated in its downward course the method would not be suited for more than about two floors, and the drying in the lower room would be cool and gentle.

One or two points in the practical arrangement of steam-pipes may be mentioned, as they are often overlooked even by professional engineers. The steam must *always* be admitted at the highest point in the system, and there must be a steady descent, without hollow places where condensed water can accumulate, to the steam-trap by which it is removed. In horizontal pipes, about 1 inch descent in 10 feet is sufficient. If water accumulates there is not merely serious danger in case of frost, but during use a vacuum is frequently formed by the sudden condensation of the steam, into which the water is shot like the liquid in a "water hammer," producing violent and noisy concussions, and in some cases even fracture of the pipes or loosening of their joints. If high-pressure steam is used a very small supply-pipe will feed a considerable system of heating pipes or radiators, but with exhaust steam great pains should be taken to have pipes of ample size to avoid back-pressure on the engines. In both cases it is often convenient to arrange the pipes, not as a continuous line, in which drainage is generally difficult, but in parallels like the bars of a gridiron. With high-pressure steam there need be no fear, if the pipes are kept clear of air by allowing a little escape through small air-taps, of the steam failing to find its way to all parts of the pipe, as a vacuum is produced by condensation in proportion to the heat given off. With exhaust steam no steam-trap is desirable, but any steam not condensed should escape freely into the open air or a chimney (after separating condensed water), and it is well to render the resistance in all the pipes of a gridiron approximately equal, which may be done by admitting steam at one corner and allowing it to escape at the opposite (diagonal) one. In the arrangement of steam-pipes in parallels the practicability of repair to one pipe or joint without interfering with the others must always be considered. If screwed wrought-iron pipes are used each parallel must be provided with a bolted flange, or "running socket," to permit of unscrewing. The difficulty of accurately adjusting the lengths of the several parallels must be considered, especially with flanged metal pipes, and also their motion by expansion when hot, which amounts to 1 or 2 parts per 1000 of length according to the temperatures of steam and air. Expansion joints with stuffing boxes are costly and troublesome and apt to leak, and may in many cases be avoided by suitable arrangement of the pipes. Thus instead of having the pipes rigidly fixed at both ends one end of the system may be left free to move, each pipe being separately returned to an exit pipe at the same end but lower in level than the supply; or a single exit pipe may be thus returned, its expansion and contraction being practically the same as that of the heating pipes. In moderate lengths of wrought-iron pipe sufficient relief may often be obtained from the flexure of the pipe if in some part of its course it is carried at right angles to its general direction, which is often necessary for other reasons. If pipes are laid in long lengths, the loose end should be supported on rollers or short pieces of pipe, so as to avoid moving the supports or straining the pipe in expansion.

It is useless to attempt to regulate the temperature of low-pressure steam-pipes by turning down the steam, since, so long as the pipe is supplied with sufficient steam to fill it, its temperature cannot be less than 100°, and even with high-pressure pipes the power of regulation by altering the steam-pressure is very limited. It is far better to arrange the pipes or radiators in groups, from some of which the steam can be turned off entirely when less heat is needed. It must not be forgotten that if these discharge into a common steam-trap it will be necessary to turn off their exits as well as their steam supply, or steam will come back into them from the other pipes, and probably prevent the escape of condensed water. In many cases it is more convenient to give the several sections independent exits or steam-traps.

Many good steam-traps are now on the market, depending either on the expansion and contraction of metals, or on floats in a closed box, which open a valve as the water accumulates. Traps of the latter class with closed copper balls are to be avoided, as the ball is sure eventually to become filled with water. Several traps have been devised in which an open vessel is used as a float, which is always kept empty by the discharge of the water through a pipe dipping into it.

The condensed water from steam-pipes is rarely suitable for use in the tannery, from the dissolved and suspended iron oxide which it contains, from which it can only be freed by boiling and filtering or treatment with precipitants (p. 67). Its most appropriate use is generally return to the boiler. Systems were formerly in vogue by which it was allowed to run back to the boiler as it condensed, but these could only answer when the pressure in the pipes was equal to that in the boiler, which is rarely the case. It must generally be forced in by the feed-pump or injector.

Hot water has often been advocated in preference to steam for heating, but is more costly, as it requires a separate boiler and much larger pipe-surface for the same effect. Its only important advantage is that the pipes maintain their heat for some time even when the fire has gone down, while steam-pipes cool at once if steam is allowed to go down in the boiler. In any considerable tannery, however, this will seldom or never be the case, since if a good pressure of steam is up at night when the fires are banked up, the boiler will in itself contain a large reserve of heat, and, of course, working pressure will be required before the engines can start in the morning. Hot-water systems require careful planning to obtain reliable and uniform circulation.

A heating system is in use in which water at high pressure and temperature much above boiling point is circulated by a pump in thick wrought-iron pipes of very small internal diameter. In the only case which came under the writer's observation it was not very successful, and if the pipes become choked from any cause, they are extremely difficult to clear. In ordinary hot-water systems without forced circulation the higher the heating pipes are above the boiler the better will be the flow.

Among other leather-drying appliances, the "automatic dryer" of Mr A. N. Marr of Leeds must be mentioned. This consists of a long chamber in which air, warmed in side chambers, and with arrangements by which the proportion of fresh air to that already used can be regulated, is circulated. From end to end of the drying chamber pass endless chains slowly moved by wormgear, which carry the hides suspended from laths, which are picked up automatically at the entrance and dropped at the exit, the heat and air circulation being so regulated that they come out dried at the farther end. The writer has seen only one of these appliances in action, which was drying chrome-tanned stock very satisfactorily, but was rather too rapid for vegetable tannages, a defect which could easily be remedied by a longer chamber and less intensive drying. The apparatus is shown in figs. 114, 115, and 116.

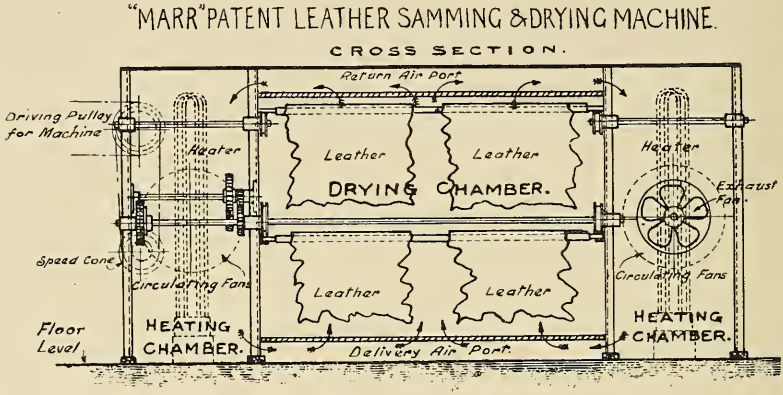

FIG. 114.

Another arrangement which fulfils the same purpose very satisfactorily, though less automatically, is to suspend the goods from laths which rest on overhead bearers passing from end to end of a long drying room through which warmed air is blown or sucked by a screw-fan. The goods are entered at the cool or exit end (for the air) and gradually advanced by hand towards the source of heat, where they are sufficiently dry for the succeeding process. Sole butts can be brought in direct from the yard at the cool end and delivered at the other ready for rolling, and the labour of advancing by hand is very small.

Another good method of artificial drying is on the principle of the Sturtevant drier, in which a heating chamber and a pressure (centrifugal) fan are conveniently combined in one machine. Of course this is by no means essential. The air may be heated in any convenient chamber by steam or any available source of waste heat, or even by a coke stove or "calorifere," and propelled by any suitable fan, but the essential difference from the systems which have been already described is that it is distributed throughout the drying room by pipes, generally of sheet iron, and about 8 to 10 inches diameter, and discharged directly on the suspended leather. These pipes may be either on the floor or, if the ceiling is a tight one, just below it, and the latter is, where circumstances permit, the better way, as the warm and dry air floats on the top of the cooler

"MARR" PATENT LEATHER SAMMING & DRYING MACHINE

SIDE ELEVATION

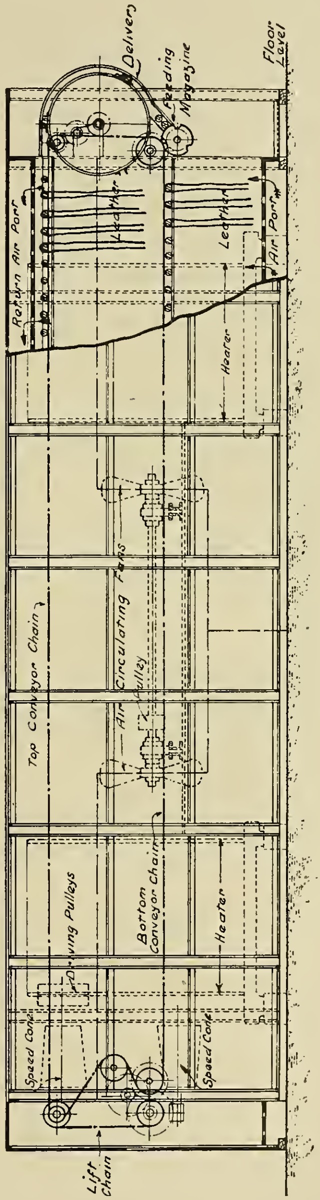

FIG. 115.

and damper and carries it down regularly below it, while warm

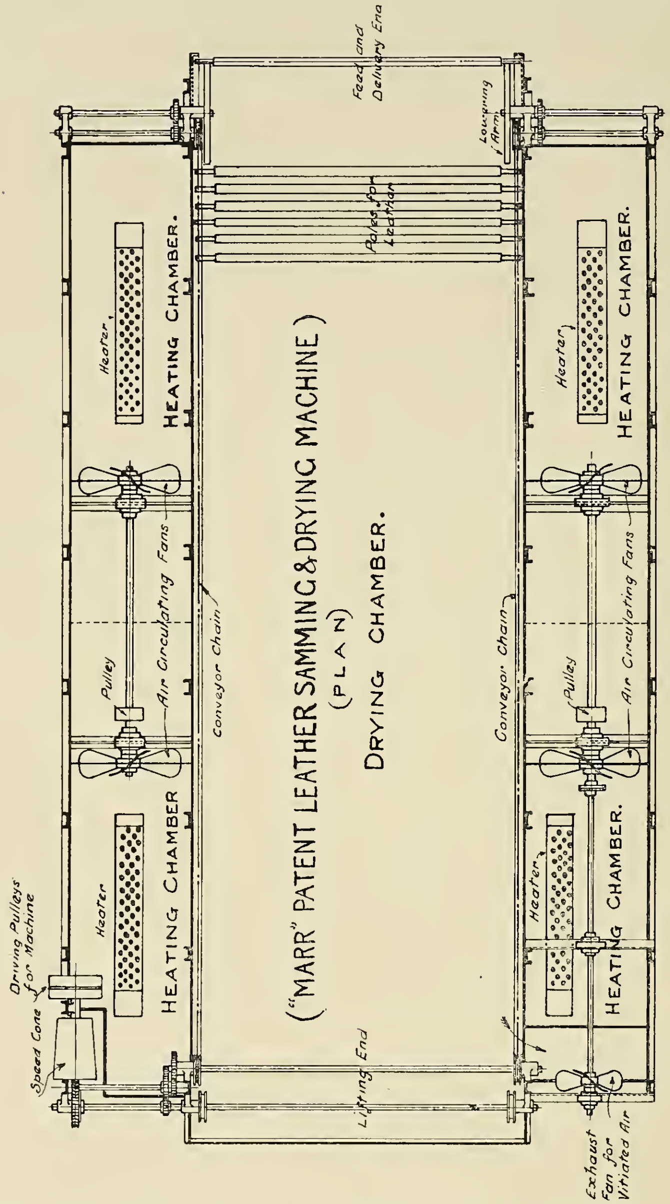

Fig. 116.

air rising through wet leather is apt to get chilled and form irregular downward currents. It is necessary that the air as it escapes from the pipes should be distributed, and this is sometimes done by small free-running fans over circular apertures in the tubes driven by the escaping air. Small perforations in the tubes will of course fulfil the same purpose, and a simple and adjustable device would seem to be a circular metal plate supported over (or under) a round aperture in the tube by a screwed central bolt on which its position could be fixed by two check-nuts. The possibility of adjustment is somewhat important, for, unless both the size of the tubes and the power of the fan is very ample, the pressure will fall off toward the farther end of the system, and the goods there will get insufficient air. Centrifugal fans are essential, as screw-fans will not give sufficient pressure to overcome the friction in the comparatively small tubes, and, for reasons which have been already explained, it is necessary to provide means for regulating the proportion of fresh air to that which has been previously passed over the leather. One of the great advantages of the Sturtevant principle is its easy applicability to most existing buildings.

CHAPTER XXX

CONSTRUCTION AND MAINTENANCE OF TANNERIES

As few architects have specially studied the construction of tanneries, and in most cases much of the arrangement depends on the knowledge of the tanner himself, a short chapter on the subject will not be out of place.

In the selection of a site a clay or loamy soil is to be preferred to a gravelly or sandy one, as lessening the liability to leakage and waste of liquor. Perhaps, however, the first consideration of all is the possibility of drainage and disposal of effluent waste liquors and washing waters, since it is now rarely possible to run these, without previous treatment, into a river or stream. Some information is given in Chapter XXXI. on the methods of partial purification which are available to the tanner, but these are always costly and troublesome, and the possibility of running direct into a sewerage system or a tidal river is of great advantage. Under the Public Health Act authorities are bound to receive manufacturing effluents into their sewers if the latter are of sufficient capacity and the effluents not such as either to damage the sewers or interfere with the processes of purification adopted by the authority. This Act is in many districts practically superseded by special legislation, but tanners' effluents are generally received into sewers if freed from solid matter. When mixed with other sewage they do not interfere with irrigation or bacterial treatment.[1] In selecting a site within a sewered district, regard must be had to the possibility of causing a nuisance to the neighbourhood by foul smells. Really injurious smells should not be caused by a properly conducted tannery, but it is difficult to avoid odour, and a single badly disposed neighbour may cause infinite trouble and expense. Traditional rights are not to be depended on as a defence, as objectors may claim that a change of process, or of the arrangement of the tannery, is not covered, even if it is really an improvement.

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[1] Perhaps in this respect arsenical lime-liquors are an exception, but the use of arsenic sulphide can now be dispensed with, substituting calcium sulphydrate or a mixture of sulphide of sodium and calcium chloride.

Another important consideration is the water supply, since for the large quantities used in a tannery, town water is generally very expensive. With regard to quality and impurities of water information may be found in Chapter VIII., but, as a general rule, the softer and purer the supply the better. It is also a great advantage when the source is at such a level that the water can flow into the tanyard, or at least into the beam-house, without pumping. Filtration too, when needed, is much facilitated by a sufficient head of water. Well-waters usually have the advantage of low and constant temperature, but are often hard.

Commercial facilities, such as nearness to markets and sources of supply of raw materials, and the availability of rail and water carriage, are of an importance at least equal to the points already considered, but hardly come within the scope of this work.

The site chosen, the next question is the arrangement of the buildings. It is very doubtful, where ground is not inordinately expensive, whether it is wise to erect drying-sheds over the pits. In case of fire very serious damage is done to liquor and leather by the heat and burning timber. If the turret form of drier be decided on, strong foundations are required, and the ground-floor or basement is occupied with heating apparatus ; if fan-drying, no lofty buildings are needed, and the drying rooms are conveniently placed over the finishing and currying shops ; and, on the other hand, the tan-house may be easily and cheaply covered with slated or felted roofs, with nearly vertical sections of glass, to the north if possible, like a weaving-shed, through which sufficient light for convenient work and cleanliness is admitted. The direct rays of the sun should be avoided, but in the writer's opinion the balance of advantage is largely in favour of a liberal supply of light. Iron roofs are unsuitable, since the moisture condenses on and rusts them, and particles of oxide fall into the liquors and cause iron stains.

Good ventilation along the ridge of the roof should be provided wherever any steam or hot liquor is used, or the condensed moisture soon leads to decay.

In arranging the general plan of the buildings much depends on local circumstances, but as far as possible they must be so arranged that the hides and leather work straight forward from one department to another with as little wheeling or carrying as possible ; that the buildings where power is used be near to the engine so as to avoid long transmissions, which are very wasteful and costly ; and that the different buildings be so isolated as to diminish the risk of the whole being destroyed in case of fire.

A chapter on the construction and maintenance of tanneries and leather works would be incomplete if it did not refer to the very important question of Fire Insurance.[1] To an extent this may be regarded as a fixed charge against any business, very much in the same way as local and imperial rates. It is not, however, to be lost sight of that to some considerable extent the amount of insurance premium is regulated by the insured himself. If a man conducts his business in unsuitable and badly constructed buildings, if attention is not paid to some of the elementary hazards connected with a fire outbreak, he must not blame the insurance companies for the demand of what he considers an excessive premium. If this faulty construction and imperfect equipment of buildings pertain to any considerable extent throughout a given trade where the process is more or less hazardous, it is futile to appeal to insurance companies, which, after all, are merely commercial and not charitable institutions, for a reduction in the rates. The only standard to guide the company is the loss-ratio, and given a high loss-ratio, there must be a corresponding premium paid.

There is, however—thanks to modern science—a method available whereby the great bulk of fires may be checked in their inception, an appliance automatic in its operation and of proved efficiency. This appliance is known as the "sprinkler." A system of water-pipes is fixed under the ceilings of the building to be protected, to which are attached sprinkling jets at suitable intervals, each of which is closed by a valve held in place by a joint of fusible metal, which gives way if the temperature rises beyond a given point. Water under sufficient pressure must of course be available. There are two or three recognised patterns approved by the Fire Offices Committee after patient investigation and practical test. These appliances have now been at work for many years in this country. One of the first trades to recognise their utility was that of the cotton-spinner. At one time serious fires in the cotton trade were of frequent occurrence. Now—owing to the efficient fire appliances—while fires may be as frequent in their inception as formerly, they are stopped at such a stage as to prevent any considerable loss. The consequence has been that the cotton-spinner, at one time the owner of a highly-rated risk, and one which few companies cared to insure, is now in the position of having his business eagerly sought for, and large discounts offered him off the charges he was once called upon to pay.

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[1] With regard to fire insurance, I am much indebted to Mr A. W. Bain of Leeds for valuable information.

More important still is the consideration to him that his business is not so liable to be interfered with or stopped as the result of fire. There are, it is estimated, at the present moment no less a proportion than 90 per cent. of the cotton-spinners whose premises are protected by sprinkler installations.

Other hazardous risks such as corn-millers', woollen and worsted manufacturer's, saw-miller's, engineers', are adopting these appliances freely, and it is a matter of surprise that so very few tanneries or currying shops have done the same. The consequence is that the loss-ratio in tannery risks still retains its unenviable notoriety ; the rates for fire insurance have risen considerably, and as a result the tanners' profits are correspondingly less. Considering the extent and importance of many of the tannery risks throughout Great Britain, one can only express surprise that these appliances have been so little adopted. There is of course risk of damage by water, which should be covered by the policy.

The construction of a new tannery demands serious attention from an insurance standpoint. The boiler-house should be a detached building ; the grinding of bark and myrobalans should be conducted in buildings isolated from the general works ; in fact no better advice could be given to a tanner, either in the construction of new premises or the rearrangement and remodelling of old, than to consult an experienced insurance man, whether official or broker, as to the best means of constructing and arranging to secure the most favourable terms.

Another point which should be provided for, and which is often overlooked, is the feasibility of future extension without serious changes of arrangement. It may be taken as a probability of the future, even if it be not already a fact, that small tanneries cannot be made to pay, and that if a business succeeds, its extension will prove desirable ; and in an ill-planned yard this may involve either entire reconstruction of a very expensive and inconvenient sort, or the separation of new departments, so as to involve serious increase of carrying. A good arrangement is that of a long front building serving to connect the whole, behind which the various departments are erected at right angles, leaving room for extension backwards as required.

As regards the carrying of goods, if the various soaks, limes, bates, and handlers are well arranged, it is hardly necessary to do more than draw the goods from one pit into the next throughout the whole of the process. To and from the layers the goods must generally be carried or wheeled. In the sheds, if it be a sole leather tannery, the butts should first come into turrets or open sheds for the rough drying, then into a room sheltered from draughts to temper for striking. The striking machines or beams should be in an adjoining room, or immediately below; then a small shed-space for drying before rolling; next the roller room; and then the warm stove for drying off. If two of the latter can be provided to be used alternately it will allow the goods to be aired off without taking down, and they may then be immediately handed or lowered into the warehouse without fear of over-drying, which is sometimes difficult to avoid where leather must be taken direct out of the hot drying room. The same principles are easily applied in yards for lighter leathers.

To lessen loss of power in transmission the engine should be near the centre of the main range of buildings, with perhaps the grinding machinery on one side and the leather finishing on the other; but this would be rather liable to increase the fire risk. A very good plan would be to have the engine-house in the centre as suggested, but separated from the buildings on each side by brick gables, and with the boiler-house behind it, and under a separate roof, say of corrugated iron. If it be impossible to have the engine near its work, it is in most cases better to employ separate high-pressure engines, which may be within a glass partition, and will work all day with scarcely any attention. The loss of power in carrying steam for moderate distances through sufficiently large and well-clothed pipes is much smaller than that of long lines of shafting. The writer has known cases where fully half the indicated power of the engine was consumed in friction of the engine, shafting and belts. High-pressure engines are as a rule to be preferred to condensing for tannery use, since the waste steam can generally be employed for heating, and both the first cost and that of maintenance are smaller. Where much fuel is used, it is quite worth while to have the cylinders indicated occasionally, both running light and driving the machinery; much information is gained in this way as to the power spent on the various machines, and very frequently large economy is effected by proper adjustment of the valves. To work economically an engine should be of ample power for all it has to do, and adjusted to its work, not by lowering the pressure of steam or by checking it at the throttle-valve, but by setting the slide-valves to cut off as early in the stroke as may be. As to how early this is possible an indicator-diagram will at once give information. If the whole of the waste steam can be used profitably for heating purposes economy in the working of the engine is of little consequence, but, otherwise, it is very injudicious, for the sake of a little saving in first cost, to put in an old or inferior engine, which has to be dearly paid for in waste of fuel. In the choice of an engine the advice of an expert engineer is desirable, since many engines which are mechanically well made are uneconomical through the faults of a rule-of-thumb design. In this respect the English engine-builder is frequently inferior to his better-trained continental competitor.

In place of using small steam-engines to distribute power electric driving deserves consideration, and in many cases power can be much more cheaply obtained from electric supply companies than it can be generated on the premises. For long drives the loss of power is much less than that of shafting, and by concentrating the whole production of the power in one large and well-constructed engine the cost per horse-power can be much reduced. While large and well-constructed engines may develop 1 horse-power at a cost in coal of less than 1½ lb. per hour, it is not uncommon to use 12 lb. for the same output. In tanneries, however, the power used bears a much less proportion to total expenses than it does in the textile and many other trades. The first cost of electric driving is somewhat high. Motors of the "armoured" or iron-cased type must be used in all positions where they are subject to wet or dust. It must be borne in mind that an electric motor will not start against a heavy load, as it only develops its full power at a high speed, and if it receive the full pressure of the current before this is attained, its coils will probably be burnt out, unless saved by the melting of its safety-fuse. A similar danger is incurred if the motor is brought up by overloading while the current is on. It is therefore often necessary to connect a motor with its work by a belt which is only brought on to the working pulley when its full speed is attained, but many motors are now made with a high initial "torque," and switches are always used by which the full power can be gradually applied.

In some cases the use of gas- or oil-engines is convenient and economical; for though gas from town supplies is an expensive fuel, the best gas-engines give a higher mechanical efficiency than steam-engines, and they work with very little attention.

In arranging shafting, moderate speeds, say 100 to 150 revolutions per minute, should be chosen for main lines, and when higher speeds are necessary they should be got by light and well-balanced countershafts, with wrought iron or wooden pulleys (*cp*. p. 545). In calculating speeds it must be remembered that they vary inversely as the size of the pulleys. Thus a 3-f. pulley running at 100 revolutions will drive a 2-f. pulley at 150 revolutions, and a 12-inch one at 300. Of course the higher its speed the more power any given shaft will transmit, but increased friction and wear and tear soon limit this advantage. The velocity of a belt in feet per minute is obtained by multiplying the number of revolutions per minute by the girth of the pulley in feet or by its diameter multiplied by $3\frac{1}{7}$, or, more accurately, 3·1416.

Pulleys should always be of ample breadth for the power they have to transmit; and it is more economical, both in power and cost, to use broad single belting than the same strength in double. If the pulley will not take a belt broad enough for the work it has to do, a second belt may be made to run on the top of the first, as suggested by Mr J. Tullis, and will do its share of the work. Belts should be washed occasionally with soap and tepid water, and oiled with castor or neatsfoot oil, but if of sufficient breadth, should not require the use of rosin or adhesive materials to make them grip the pulley. Chrome-leather belts should be kept thoroughly oiled. They have a much greater adhesion than vegetable tannages, and this is increased by oiling. Good chrome belting is much stronger than bark-tanned, and is unaffected by damp or steam, but generally stretches somewhat more. Makers of machines often err in constructing their driving pulleys too small both in breadth and diameter. Very thin or soft belts will not run satisfactorily on flanged pulleys, as the edges turn up, and the belt often becomes crooked. This trouble is often due to pulleys not being in proper alignment, as the belt then tends constantly to run against the rigger to one side. Pulleys should always be *slightly* higher in the centre than at the edges, as the belt tends to run on the highest diameter.

The horse-power which a belt is capable of transmitting obviously varies extremely with circumstances, but may be approximately calculated by the formula $\frac{a \cdot v}{66000}$, where a is the area of contact of the belt with the smallest pulley, and v its velocity in feet per minute. Another rule is, that at a velocity of 1000 feet per minute each inch of breadth of belt should transmit $2\frac{1}{2}$ horse-power on metal pulleys, or 5 on wooden ones, on which the adhesion is greater. Adhesion may also be increased by covering the pulleys with leather or indiarubber, but in the latter case oily belts cannot be used. Holes are sometimes drilled in broad pulleys to allow of rapid escape of air. Both rules assume that the belt is of ample strength. One horse-power would be transmitted by a belt running 1000 feet per minute with a pull of 33 lb. A good single belt should not break with much less stress than 1000 lb. per inch of breadth, and should not be given more than one-tenth as much as a working stress.

The following table gives the experimental breaking stresses and extensions of some leathers. It may be noted that 1 square inch sectional area is equal to a belt 4 inches wide by $\frac{1}{4}$ inch thick, and that *kilos per cm.*$^2 \times 14{\cdot}22 =$lb. per inch.

Breaking Stresses of Leather[1]

	Kilo per sq. centimeter.	Lb. per sq. inch.	Stretch per cent.
Belting leather, layer system .	283	4,030	25·4
,, ,, Durio system .	298	4,240	21
Well-tanned chrome leather .	740	10,500	32·5
Over-tanned chrome leather .	234	3,330	23
Stuffed alumed leather . .	835	11,900	38·3
Alumed "rawhide" . . .	921	13,100	31·4

Good English-tanned belting leather breaks at from 4500 to 5500 lb. per square inch sectional area.

Over-tanned leathers are less tough (though they stretch less), whether of vegetable or mineral tannage, than those somewhat lightly tanned, and the tensile strength of leather varies considerably with the part of the hide from which it is taken, that from approximately over the kidneys being the strongest. Even thick and tough leather is easily torn if a cut or nick is once started, and all holes used in jointing belts should be carefully rounded. Glucose and the use of acid in bleaching both lessen the toughness of belts, and they may also be rendered tender by the heat evolved in slipping on a pulley.

Countershafting and high-speed machinery, such as disintegrators, striking machines of the Priestman type, etc., should run without material jar or vibration. If this occurs, it is generally a sign that the rotating part is not equally balanced. In this case the shaft or spindle must be taken out of its bearings and supported on exactly horizontal straight-edges, on which it will roll till the heaviest part is downwards, and weight must then be taken off or added till it will lie in any position. In this way the writer has had to add fully 2 lb. of iron nuts to balance the drum of a striking machine before equilibrium was secured and a most troublesome vibration prevented. The exact alignment of bearings is very important, and a shaft running in bearings out of line will ultimately break. Of course all machinery should be supported as solidly as possible; and if circumstances permit,

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[1] Gerber, 1900, p. 73.

most machines are better on a ground floor. In placing bark mills, however, it is frequently convenient to fix them at a higher level, so that the ground material may be sent down shoots by its own weight to the required places. An alternative, and perhaps better, plan is to set the mill on the ground over a pit, and to raise the ground material with a bucket-elevator. This may be done successfully by letting the material fall directly from the mill into the buckets ; but otherwise it must be thrown in with a shovel, as buckets will not pick up ground bark, even from a hopper ; and in any case such elevators are apt to be troublesome, the tanning material getting between the pulleys and the belt, and causing the latter to break or come off. In a grinding plant designed by the writer the unground material was filled on the basement floor into an iron barrow, which was wheeled into an iron sling working between upright guide-rails like a hoist. On pulling a brake line the barrow was raised to the top of the building, and its contents were tipped into a large hopper, after which the barrow righted itself, and descended for another load. In the bottom of the hopper was a sliding shover, which forced the material on to vibrating screens, by which it was guided either into a disintegrator or crusher-rolls at pleasure. Both these discharged through iron spouts into large hoppers on the outside of a brick gable, from which powdery materials like myrobalans and valonia could be run direct into barrows or trucks. It is very desirable that such hoppers should be separated from the main building by a fireproof partition. Fires may occur from hard substances getting into disintegrators along with the bark, etc., and if this occur with a dry and dusty tanning matterial, it is not unlikely that it may result in an explosion such as sometimes happens in flour mills, in which the fire is rapidly conveyed along spouts and into chambers filled with dusty air. Insurance companies generally charge an extra rate for disintegrators, and it is very desirable to keep the mill-house structurally apart from other buildings, either by actual separation or by the introduction of brick gables *dividing the roofs.* On the whole, however, mills of the coffee-mill type are probably quite as dangerous as disintegrators, since if they become partially choked, the heat caused by friction is very great.

In America the fire risk from mills is often lessened or prevented by the introduction of a jet of steam into the chamber or spout by which the mill discharges, but this is only permissible if the tanning material is conveyed at once to the leaches or yard.

The use of chain-conveyors for handling tanning material, both wet and dry, is practically universal in America, though comparatively rare in England. Various forms are used, the most common consisting of a chain of square links of malleable cast iron which hook into each other, so that a broken link can be immediately replaced (see p. 389). At intervals special links are inserted, which can be had of various patterns, for the attachment of scrapers or buckets. The endless chain runs in a trough of rectangular or **V**-shaped section, and is driven by a toothed wheel, over which it runs like a belt. In some cases the returning half of the chain can be utilised to bring back the spent tan on its way to the boiler-house. For dry materials, cotton or leather belts working in troughs with short wooden cross-laths attached may often be used satisfactorily in place of the chain. The laths should be slightly wider than the belt.

For lubricating purposes mineral oils of high density are not more dangerous than animal or vegetable, but rather the reverse ; as, though they are possibly more inflammable, and make more smoke, their mixture with cotton-waste and other porous materials is not spontaneously combustible, as those of vegetable and animal oils occasionally are. The danger of spontaneous combustion is very considerable when heaps of leather shavings or cuttings containing fish-oils are allowed to accumulate in warm workshops, and especially near steam-pipes. Heavy mineral oils should always be used as cylinder-oils in high-pressure engines in preference to other oils or tallow, since they are not decomposed by steam, and do no harm if blown into the feed-water, but serve to loosen and prevent scale and deposit. Ordinary oils and tallow, on the other hand, when submitted to the action of high-pressure steam, are separated into glycerin and fatty acids (see p. 428), and the latter corrode the valve faces and seatings, and are liable with " temporary hard " waters to form a very dangerous porous deposit in the boilers, which often leads to overheating of the tubes.

Next to the machinery the pits demand special consideration. The chapter on the subject in the late Mr Jackson Schultz's book on *Leather Manufacture*, though now rather out of date, is well worth attentive study as giving American practice on the subject.

The old-fashioned method of sinking pits is to make them of wood, and carefully puddle them round with clay, which should be well worked up before use. It is of no use to throw it in in lumps and attempt to puddle it between the pits, which will not be made tight, but probably displaced by the pressure. Such pits, if made of good pine and kept in constant use, are very durable, some of the original pits at Lowlights Tannery, constructed in 1765, having been in use till 1889. Loam mixed with water to the consistence of thin mortar may also be employed, the pits being filled up with water, to keep them steady, at the same rate as the loam is run in. One of the best materials for pit sides are the large Yorkshire flagstones. Where these are not attainable, very durable pits may be made of brick, either built with Lias lime and pointed with Portland cement, or built entirely with the latter. Common lime cannot be used, as it spoils both liquors and leather ; and even cements with too large a percentage of lime are unsatisfactory. Brick and common mortar are, however, suitable for lime-pits, and for these Mr C. E. Parker's plan of constructing the bottom of cement, the ends and sloping hearth of brick, and the sides of 3-inch planks bolted together is also very satisfactory (fig. 117). Most of these methods are now, however, superseded by reinforced concrete.

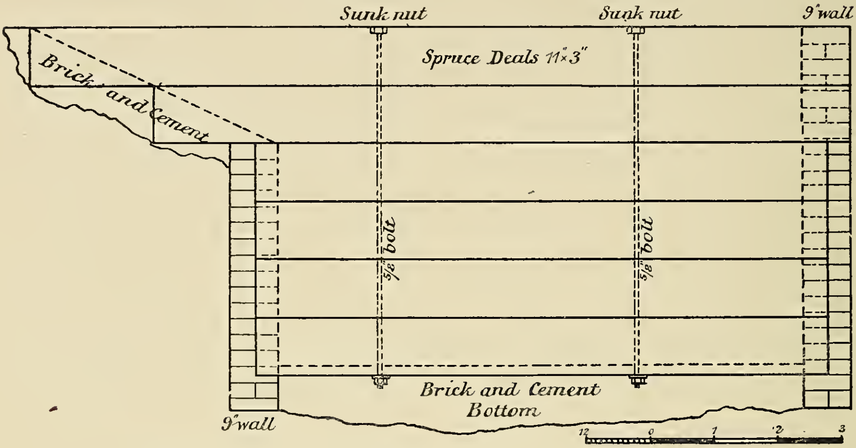

FIG. 117.—Mr C. E. Parker's construction of Lime-pits.

The writer has constructed wooden pits in two ways. In the one case, after making the excavation, beams were laid in a well-puddled bed of clay ; on these a floor of strong tongued and grooved deals was laid, and on this the pits were constructed of similar wood to the floor, and puddled round with clay. In the second case the pits were built like large boxes above ground, and when finished lowered on to a bed of clay prepared for them, and then puddled both around and between. It may have been due to defective workmanship in the first case, but those made on the last-named plan, which is that adopted from very early times, certainly proved the tightest and most satisfactory. Mr Schultz describes a plan as the Buffalo method, in which a floor is laid as just described, and grooves cut with a plane for the reception of the sides, which are formed of perpendicular planks, each end and side being finally tightened up by the insertion of a "wedge plank." Owing to the perpendicular position of the side planks such pits would be difficult to repair in the common case of decay at the top.

If bricks be used, great care must be taken that the cement is not merely laid so as to fill the joints towards the two surfaces of the wall, as is the habit of modern bricklayers, but actually floated into all the joints so as to make the wall a solid mass, or leaks can hardly be avoided. Hard-pressed bricks are best, and should be tested as to whether they discolour liquor. Cement-pits are very good, and though not particularly cheap in material, which must be of the best, are readily made by intelligent labourers under good supervision. The first step is to lay a level floor of good concrete, in which glazed pipes for emptying the pits may be embedded, care being also taken that all joints in these are thoroughly tight, since future repairs are impossible. The next step is to make frames the exact length and breadth of the pits required, and perhaps 15 inches deep. These are arranged on the floor where the pits are to be, and the intervening spaces are filled with concrete of perhaps one of cement to three or four of crushed stone or brick. Rough stones and bricks may also be bedded in the concrete as the work goes on to help to fill up. After the first layer has set, the frames may be raised and a second added, and so on. The work is generally finished by floating over it, while still damp, a little pure cement to give a smooth surface. Before using, the cement should be tried on a small scale to be sure that it does not discolour leather or liquors, and the pits should always be seasoned with old or cheap liquor before actual use.

If possible, both leaches and handler-pits should be provided with plugs and underground pipes communicating with a liquor-well some feet below their levels. Glazed fireclay is very suitable for both pipes and plug-holes, which should be in the pit corners. If fireclay blocks for plug-holes cannot be obtained, they may be cast in good cement, the wooden mould being soaked with hot paraffin wax to prevent adhesion. Means must be provided for the ready clearing of the pipes when choked with tanning materials. A good plan is to let each line of pipes end in a liquor-well large enough for a man to go down. As it is almost impossible to make plugs fit without occasional leakage, it is not well to run pits with very different strengths of liquors to one well, but the layers, handlers, and different sets of leaches should each have their own so as to avoid mixture. A good means of clearing pipes consists in a series of iron rods 3 to 4 feet long, connected by hooks fitting into double eyes, as shown in fig. 118. It is obvious that in a narrow pipe or drain these cannot become disconnected. The ordinary canes of the chimney-sweep are also useful. Pipes may often be forced out by fitting a strong delivery-hose of a steam-pump into one of the plug-holes.

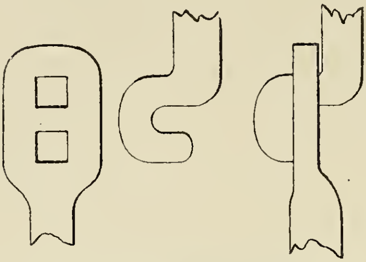

Fig. 118.—Cleaning Rod Joint.

It is, as Schultz points out, of questionable advantage to lay wooden troughs under the alleys for supplying liquor to each pit, since it is almost impossible to preserve them from decay, but the same objection would not apply to glazed pipes jointed with pitch or cemented. Between concrete-pits the alleys would probably also be concrete. A very fine tar-macadam, such as is often used for footpaths, seems also suitable for alleys, and is easier to take up and make good for repairs of pipes than cement. A good and cheap plan in practice is to let the liquor-pump, or a raised liquor-cistern, discharge into a large and quite horizontal trough raised 6 or 7 feet above the level of the yard, and provided with plug-holes at intervals, from which the liquor can be run into the various pits by short spouts or sail-cloth hose. In place of plugs in the raised trough a simple and convenient valve devised by the writer may be advantageously employed. A lead weight is made by casting in a hemispherical pressed steel basin of about 5 inches diameter and 2 inches deep in the centre, a loop of strong brass wire with turned up lower ends being suspended in the middle so as to become fixed in the lead. To prevent adhesion the tin must be previously burned off and the basin well black-leaded. This weight forms the valve, which rests in use on a 6-inch washer of good indiarubber with a 4-inch hole, which is held by a wood block or brass flange against the bottom of the trough, through which a 5-inch hole is cut. The valve is raised by a lever or cord, and is absolutely water-tight in use. It is shown in section in fig. 91 (see p. 397).

It is very advantageous in practice, instead of pumping direct into the pits, to have one or more tanks into which liquor can be delivered by the pump, and which are sufficiently raised to allow it to be run from them into the horizontal distributing troughs which have been mentioned. This is specially important with regard to liquors for leaches and suspenders which are worked on a circulating system, since they do not run very quickly, and much time is lost in pumping out pits if the speed of the pump has to be regulated by the rate at which the liquor will circulate. It also enables liquors to be run through suspender- and rocker-pits during the night or at meal-times while the machinery is standing; and it is often useful on beginning work in the morning to have an empty tank into which the first liquor can be pumped.

Pumps.—Direct-acting steam-pumps without fly-wheels are very unsatisfactory for tanyards, since they are usually uncertain in their action, difficult to run slowly, and apt to "hammer," and they are also costly in steam, which cannot be used expansively. Steam-pumps with fly-wheels, operating the steam-valve by an eccentric, are free from these defects, and though more costly at the outset, soon save the difference in lessened repairs and consumption of steam. Pumps with a capacity of 8000 gallons per hour are very suitable, and can be used with a 3-inch hose-pipe; smaller sizes are decidedly more liable to choke with tanning material. Rubber mitre-valves work satisfactorily, and do not choke frequently, but are costly, and easily damaged by hot liquors. On the whole, brass clack-valves are the most satisfactory, but the hinge-pins, instead of fitting neatly in circular sockets, should be held in slots, allowing the back of the valve to rise half an inch, when it will clear itself of small hard myrobalan stones and such-like things, which, getting under a more tight-fitting hinge, would prevent the valve closing, and so stop the pump. Rubber-covered balls working in a cage are also good. Whatever valves are employed, means should be provided for easy access without unscrewing too many bolts. If the several valve-chambers of the pump are closed by a single cover with an indiarubber washer the spaces between them which make the joint should be faced with brass or gun-metal, as, if the least leakage takes place over an iron surface, the friction and solvent power of the liquors soon eat away the metal and render a good joint impossible. Where colour is of first importance it is well to have the whole pump of gun-metal, but in any case the working cylinder should be brass-lined, and the piston and rod and the valves and seatings should be of brass or gun-metal. Spring-rings are far better than pump-leather, and are unaffected by hot liquors; chrome leather, however, will stand a good deal of heat. Double-acting force-pumps have practically superseded the older single-acting double or triple pumps. Instead of direct driving with a steam cylinder it is sometimes advantageous to drive by belt, but at least one steam-pump should be provided, so that pumping can be done when the main engine is not running, and the speed of the pump can be regulated to the work, which is impossible in a belt-driven pump. Steam-pumps are sometimes very useful as fire-engines.

Centrifugal pumps are very suitable for tannery work where the liquor is drawn from a well, but are not well adapted for use with suction-pipes. If the form with vertical spindle is adopted, which is sunk below the liquor in the well, the pump fills itself and needs no foot-valve, but unless the well is very large, or some convenient means is devised of withdrawing the pump, repair or cleaning is difficult. If the horizontal pattern is used, which is above the ground, repair, cleaning, and driving is much easier, but a foot-valve is necessary, which may itself give trouble, and some convenient means, such as a pipe from a raised tank, should be provided for filling the pump with liquor, as, unlike suction pumps, centrifugals will not start unless full, although they raise very large quantities when running, and from their steady flow will deliver much more through a given pipe than an ordinary reciprocating pump with the same power. In selecting the pump care should be taken that the pattern allows ready access, not only to the foot-valve, but to the body of the pump. Some of the more modern rotary pumps may prove suitable.

It is seldom satisfactory to use windbores or strainers to prevent tanning material getting into a pump, as they speedily become choked ; and it will be found better, after taking such precautions as are possible, to have the pump and valve of ample size and suitable construction to pass what comes with the liquor. The writer has known a mop-head pumped and delivered through a 3-inch hose without stoppage by a Tangye fly-wheel steam-pump with brass clack-valves such as have been alluded to.

Pulsometers have not, in the experience of the writer, proved satisfactory in tanneries, warming and diluting the liquor, consuming much more steam than a pump of the same power, and becoming easily choked. For the same reasons, steam-jet water-raisers are not to be recommended except where raising is to be combined with heating, as in some leaching devices (p. 400).

But little alteration has been made in the foregoing chapter since it was written in 1903, but it may be in place to conclude with a few words as to the tendencies recently observable. The use of reinforced concrete, not only in general construction but in the making of pits, has considerably increased, partly due to the difficulty of building in brick, since it is possible to do much of the concrete work with the semi-skilled labour generally available about a tannery, and with the aid of the joiners' and fitters' shops with which modern tanneries are generally provided. For the construction of pits it is probably really the most satisfactory material, and for lime- and water-pits requires no further finishing, but for liquor-pits should be coated with boiled oil, with pitch, or with some sort of varnish, though some cements withstand the action of ordinary tanning liquors quite well without. For chrome liquors protection by some varnish is essential, and cement on the whole is probably less satisfactory than wood or, what is still better, slate.

In roofing for tan-houses the weaving shed construction with lights to the north has still much to recommend it, but for lime-houses the light wooden latticed girder and curved roof has very much taken its place, as it has the advantage of giving very large spans without the obstruction of pillars. One of the finest lime-houses which the writer has seen is that of Messrs Walker at the Rosehill Tanneries at Bolton, not only on account of its size, but from the admirable arrangement of the machines, first the lime-pits with suspension and agitation with compressed air, then a row of unhairing machines with pits behind them to receive the hair, next a row of fleshing machines with pneumatic rolls, and finally a wide space for sorting and rounding, so that the hides proceed direct from the limes to the rounding table. For flooring for most purposes about a tannery good concrete is quite satisfactory, but it is a good deal attacked by acid chrome liquors, and genuine asphalt or the fine tarmac often used for footpaths would probably be more durable.

For leather drying the use of wooden louvre-boarded buildings has become almost obsolete, and brick structures with pivoted windows have largely taken their place, while drying with artificial heat and fan ventilation is almost universal. Details of the methods most in use will be found in Chapter XXVIII. The use of fire-proof reinforced concrete floors for upper stories is increasing. Compressed air is coming much into use, both for agitating and for moving liquors. Mechanically it is not very economical, as much heat is lost at the compressor, which must be water-jacketed, and the compressed air cools the liquors in expanding, which is sometimes advantageous and sometimes the reverse, and it costs as much mechanical power to force air to the bottom of a liquor as to raise the same volume of water the same height, but once the somewhat expensive compressor is installed, its convenience is so great that this disadvantage is probably fully compensated. For stirring of suspension limes the air is simply allowed to escape from perforated tubes at the bottom of the pit, of which the bottom should be so curved as to promote a good circulation of the lime and liquor, and the only trouble which sometimes occurs is the tendency of the lime sludge, which must settle towards the air-pipes, to choke them when the air is not flowing. For this reason it is probably best to have the openings directed downwards. For the stirring of tanning liquors the oxidation has been pointed out as a disadvantage, but unless the liquors are alkaline, the loss is not likely to be important. With chrome liquors no oxidation takes place, but if used for hypo liquors in the two-bath process there may be loss of sulphurous acid. For stirring loose skins, compressed air is not so satisfactory as the paddle.

The moving of liquors by compressed air is done by the " air-lift," the liquor being allowed to flow down into a well some little depth below the bottom of the pit, and the air being made to bubble up through an open-ended pipe, when it will carry the liquor up with it to some height above the surface of that in the pit. This has the great advantage over pumps that there are no valves and no wearing parts. The method has long been used in the United States for raising water from deep wells where the installation of a pump would be difficult.

CHAPTER XXXI

WASTE PRODUCTS AND THEIR DISPOSAL

THE products which are of no direct value to the tanner and currier in the manufacture of leather, and which are nevertheless obtained in fairly large quantities, are of very varying characters. In the present chapter the most important of them will be described and some of their uses mentioned.

Hair is removed from the skin of the animal in the process of depilation (p. 166) in the form of a wet sodden mass, containing a considerable amount of lime when the skin has been through the lime-pits.

As white hair is the more valuable, it is desirable in the unhairing to keep it separate from the coloured, but this cannot well be done in unhairing with machines. It is washed first in plain water to get rid of as much of the lime as possible, and then in water containing a little acid. Hydrochloric acid is often used for this purpose, but sulphurous acid (p. 24) is preferable, as it has a slight bleaching action on the hair. The acid neutralises and renders soluble the lime which still remains in the air, so that it can be easily removed by washing with water. In many tanneries hair-washing machines are used. The washed hair is dried by laying it out on frames; or preferably, the greater part of the water is first removed by a centrifugal drier or by pressing, and the drying is completed in a drying room, the temperature of which may be pretty high if it is provided with a fan or some other appliance for mechanical ventilation. Tables of wire-gauze on which the hair is spread, and through which the warm air of the room is drawn by a centrifugal fan, are very effective.

Coloured hair is sometimes washed and treated like the white hair, but is usually sold direct to plasterers, in which case there is no necessity to remove all the lime and other impurities which the hair contains. A considerable amount of hair is also sold to iron founders, who use it in preparing cores and in loam-casting. The loose lime may be effectively beaten from dried hair by passing it through a disintegrator with one of the grates removed. The use of moderate quantities of sulphide in the limes, though they weaken the hair, do not seem to affect its commercial value.

Fleshings and Glue-stuff.—The various scraps of fat and flesh, containing some actual hide substance, are usually worked up for glue, though if they cannot be sold for a fair price it will pay to boil them in order to recover the fat they contain. Before boiling, the fleshings are treated with sulphurous, sulphuric, or hydrochloric acid, sufficient to neutralise the lime present. The boiling should be carried on very gently, so as to allow the fat to rise without emulsifying with the gelatinous matter. Open steam may be used, but in this case the size formed will have little value; on the other hand, if the fleshings are carefully delimed with sulphurous acid and a wooden vat with a copper steam coil be employed, really good size may be obtained, and the slight trace of bisulphite which it may contain will prevent its putrefaction. Except under special conditions it will not pay to make glue on a small scale in England, as its value depends much on its appearance, and the necessary plant is somewhat expensive. In some places, however, size can be sold to advantage. Fig. 119 shows a glue-boiling plant.

Material for glue must be in a neutral condition. In dried glue-stuff this is secured by the carbonation of the lime in drying, but wet fleshings or glue pieces must be freed from lime by treatment with acid, preferably sulphurous, and then from excess of acid by thorough washing, which may be shortened by the use of a little soda in the last wash water, so that the material is neutral to methyl orange or Congo red, but must not redden phenolphthalein. In place of using sulphurous acid goods may be carbonated by blowing carbonic acid (the fumes of a coke stove, or even washed furnace-gases) through them in water till they no longer redden phenolphthalein, and this method is particularly advantageous with matter containing rancid fats with oxidised acids, which from their ready emulsification are particularly apt to render the glue turbid. The skimmed fat is also improved, but the "scutch" or undissolved residue must be treated with acid to recover the fatty acids present as lime-soaps. The writer has in this way made a bright glue from seal-fleshings, which usually give one turbid and nearly black.

Skin-glues are generally boiled in open vats such as are shown in the illustration. These may be of iron or copper or of wood, like the leaches used in tan extraction (p. 395), and, like them, they are furnished with a copper heater or boiling coil, and with a perforated "false bottom," usually of iron or copper, to support the material. The steam for heating is supplied by a vertical pipe in the centre, which is surrounded by a wooden casing or "eye" passing through the false bottom, so that when the liquor boils it rises through the casing and flows over the top of the vat, passing down through the glue-stuff. If dry material is to be boiled the vat is usually fitted with a "curb," in which the "spetches" can be piled, and sink down gradually as they soften. For material in which the lime has been neutralised and rendered insoluble by carbonation iron vats are quite suitable, but if acid deliming, even with sulphurous acid, is practised, wood is better, because the iron (and even copper) is slightly attacked and darkens the glue. After boiling for six or eight hours as much of the fat as possible is skimmed off, and the liquor is run into a tank, where it is allowed to cool somewhat, and a further portion of fat separates. The material is boiled a second time with a further quantity of water, and for common glues this size is usually used to fill the vat for boiling a second lot of glue material. A preferable method is to evaporate at once for a somewhat inferior glue, or to add it to the strong size for evaporation (see below). Some alum or alumina sulphate is frequently added to the size at this stage to harden the jelly and raise its melting point.

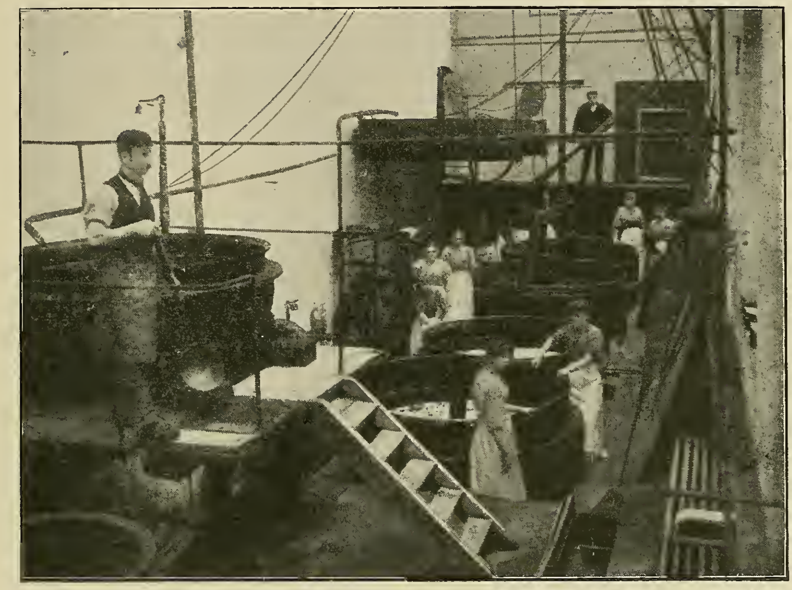

FIG. 119.—Glue Boiling.

After separation of the fat by skimming, the clear size is run off from the residual matter into wooden or galvanised iron cooling troughs about 5 feet long by 9 inches deep and 15 inches wide, in which it is allowed to set (fig. 110, p. 517). Great care is required that both size and coolers are quite sweet and free from putrefaction, the coolers being frequently washed with sulphurous acid solution or fresh milk of lime. The jelly is cut out of the coolers in blocks, and sliced into cakes of appropriate thickness by means of a series of frames like slate-frames which fit over the block of glue, and between which a wire or thin blade stretched on a saw-frame is inserted to cut the glue into sheets, or now more commonly by a machine with a series of parallel blades against which the glue-block is pushed. The sheets are afterwards separated by girls and laid to dry on nets, on which they are frequently turned. When dry the cakes may be washed with warm water to remove any adhering dirt, which in smoky districts quite spoils their appearance, but this causes some loss of weight, and in many cases it pays better to dry in a stove until quite hard, then grind in a disintegrator and sell as "size-powder," in which appearance counts for little if the colour and strength of the size are good.

Artificial heat cannot be used in drying the soft glue on the nets, and in hot, and especially in thundery, weather it sometimes melts and runs through the nets, not only wasting the material, but making a mess difficult to clean up; and bacterial troubles often occur, probably increasing the tendency to melt, and causing bubbles in the interior of the cakes. For this and other reasons the process just described has been largely superseded, and the settled or filtered size is run direct to an evaporator of the Yaryan or "Climbing Film" type (p. 408), and concentrated till it will set to a firm cake when run on glass plates previously waxed or rubbed with ox-gall to prevent its adhesion. Vacuum is not strictly necessary, as the very brief heating to boiling temperature does not noticeably injure the glue. The cakes when set are stripped off the plates and dried on nets, which are often in frames on wheels, which are passed through a "tunnel" through which warm air is circulated, entering at the farther end, when the partially dried glue can stand a higher temperature.

Fat.—The fat, whether obtained in the manufacture of glue or by boiling the fleshings and shavings for its recovery alone, is skimmed from the surface of the heated liquor, and should afterwards be freed from gelatinous matter by washing it with hot water in a tub and running off the upper layer after allowing the water to settle out. The fat thus obtained is a light-coloured grease of buttery consistence.

There are various other sources of waste fats which may be considered here. If glue is made from dried glue-stuff without previous treatment with acid, the fat skimmed off the pans, though dark in colour, will be neutral or alkaline, and a considerable additional quantity of fat and free fatty acids may be obtained by reboiling the " scutch " or refuse with open steam in lead pans with the addition of water and enough sulphuric acid to render the contents of the pan distinctly acid. The scutch may also be pressed in steam-heated presses, such as are used to extract the " magma " precipitated from wool-washings. This grease will be dark and of unpleasant smell from volatile fatty acids, but its odour may be to a considerable extent improved by blowing air and steam through it and washing with water, or by heating to a temperature somewhat above the boiling point of water for a considerable time. The same sort of treatment may be applied to the fat pressed out of sheep-skins, and to that obtained by boiling currier's shavings with water and a little acid.

Recovered fats may be separated into a tolerably firm grease suitable for use instead of tallow in currying, and an oil, not unlike neatsfoot oil, by melting, allowing to cool slowly to a soupy consistency to promote the crystallisation of the harder fats, and forcing the mixture through flannel cloths in a filter press. The temperature at which the filtration should take place is generally 20° to 25° C. The oil is, of course, " tender," or liable to solidify in cold weather, and the more so the higher the temperature at which filtration takes place, and this might be lessened by a second filtration at a much lower temperature. The tallow is obtained in cakes. If from fresh fleshings it will be white and with little odour, but that from dried glue-stuff is usually brown and of unpleasant smell, while recovered grease from curriers' shavings or " moisings " is always dark in colour.

If the fleshings are to be sold wet, they should be preserved in a sweet lime liquor ; if to be dried, they are washed carefully in a fresh lime, spread on frames, and frequently turned over so that they may dry evenly and rapidly. Heat, if employed at all, is in most cases only used at the end of the drying operation, but some tanners dry from the first in a room the temperature of which is a few degrees higher than the normal, and which is provided with good ventilation. For the purposes of the glue manufacturer the roundings and larger pieces are more valuable than the fleshings, and should be treated with correspondingly greater care by the beamsman and his assistants.

Bate-shavings are very valuable as sizing materials. They should be well washed in water, or with a very dilute solution of sulphurous acid, and are then laid out in thin layers to dry. They may also be partially dried by pressing between latticed boards in a screw or hydraulic press, and are then best finished as cakes. On the manufacture of sulphurous acid compare p. 24.

Horns are usually kept until the " slough," " pith," or internal bone can be knocked out, having become loosened through drying and putrefaction. If kept dry, practically no longer time is required, and the smell and other annoyances incidental to storing in a damp place are avoided. The sloughs may be removed at once by steaming, but the horns are somewhat damaged by this treatment. The sloughs are principally ground for " bone-meal," but some are boiled for glue, either without preparation or after decalcifying with dilute hydrochloric acid.

The actual horn itself, which is quite incapable of making glue, is used chiefly in the manufacture of combs, buttons, and similar articles. The value of horns is to a considerable extent dependent on their size, small horns being unprofitable to work up for the articles above mentioned.

Spent Tan.—The tan as it is obtained from the leaches after extraction has, naturally, no value for the tanner except as a fuel. Spent tan cannot be profitably sold as manure, as its worth in this respect is extremely small. In those places where white lead is still made by the Dutch process, oak-bark is used to cover up the earthen pots, and commands a good price. It is, however, essential that oak-bark only should be used, as many other tanning materials give off products which injure the colour of the white lead. The quantities of tan used for hot-beds, and for deadening the noise of traffic in the streets, are so small, that they are of no practical account in the disposal of this product. Spent tan is not nearly as good as wood for the manufacture of paper, though spent mimosa bark has been used for brown paper with some success. An attempt to distil it, and thereby obtain pyroligneous acid and wood-spirit, did not result in any commercial success. On the Continent fine-ground tan is usually pressed into briquettes for use as domestic fuel, but it would be hard to obtain a market for these in England.

On the whole, in spite of its low heating value, spent tan is best utilised as a fuel. For this purpose specially constructed furnaces are necessary on account of the dampness of the tan and its low calorific value, which varies, however, with the particular materials : thus while oak-bark and valonia are only poor fuels, hemlock and myrobalans are much better on account of the resins and lignine they contain.

The first successful furnaces for raising steam with wet tan were introduced in the United States, and consisted of a large arched combustion chamber with abundant grate-area, and with four or six feed-holes in the fire-brick top which formed a floor on which the spent tan was laid, and where to some extent it was dried by the waste heat. The flames and furnace gases were conducted under the boilers, the flue being very large and deep so as to collect the light ash which was drawn in great quantities from the furnace, and the gases were then returned through the tubes of the boiler, afterwards passing down the sides and going to the chimney. The wet fuel, partially dried on the firing floor, was fed in through the firing holes alternately, so that only a part of the grate-space was covered at once with wet fuel, which was speedily ignited by the heat from other parts of the furnace, and especially from the vaulted arch.[1] The large grate-area was a necessity not only on this account, but because of the light weight of the fuel and its low calorific power, which involved the need of burning a large volume. Fig. 120 represents a furnace of similar principle constructed by Messrs Huxham and Browns. Furnaces of this type are, the author believes, still largely in use in the United States, but in Germany "step-grates" sloping from the furnace-doors towards the back are now preferred. In these the combustible material rests upon the flat surfaces of the grate, while the air enters by the spaces between the steps without the fuel being able to fall through.

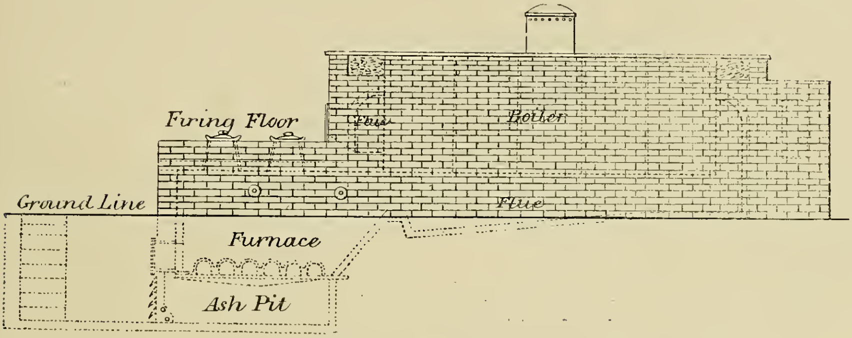

FIG. 120.—Huxham and Brown's Furnace.

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[1] Detailed drawings and particulars are given in Jackson Schultz's *Leather Manufacture in the United States*, New York, 1876.

Fig. 121 represents the furnace on this principle constructed by the Moenus Co. of Frankfort.

The essential conditions which are to be observed in the proper burning of the tan are a sufficiently large grate-area, a correct and sufficient supply of air, and a combustion-chamber of very high temperature. It is consequently not possible to burn tan very successfully in an ordinary Lancashire or Cornish boiler, since not only the grate-space is too limited, but the water of the boiler prevents the upper part of the furnace from attaining a high temperature, and it is therefore difficult to get the damp tan rapidly into vigorous combustion. The difficulty may to some extent be overcome by mixing the tan with a proportion of coal, and by closing the ash-pit and employing a forced draught, unless the chimney is a very powerful one. In this way large quantities of tan may be burnt, but without effecting any great saving of coal. The heating power of the tan is improved by the partial removal of its water by pressing, and this is almost essential where a special furnace is not employed.

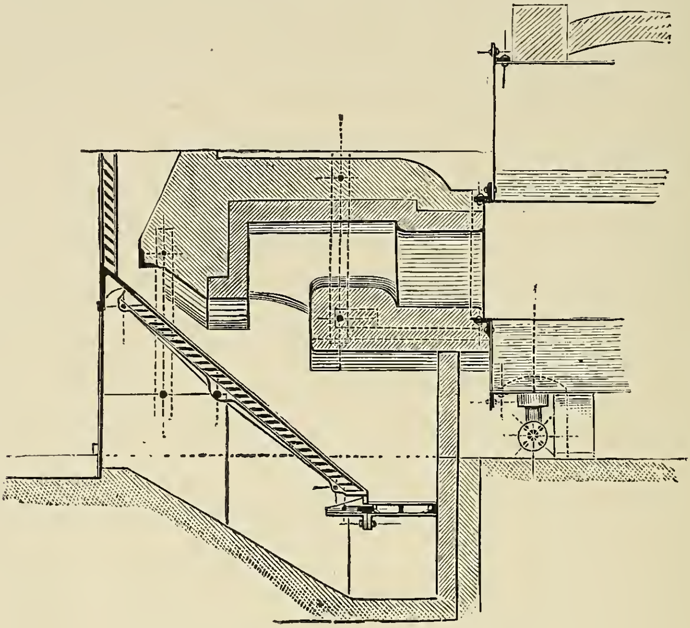

Fig. 121.—Moenus Step-grate Furnace.

The answer to the question as to whether tan should be used as fuel in the wet state in which it is obtained from the leaches, or whether it should be previously pressed, depends upon the nature and quantity of the tan. Where abundant quantities of a fairly good material such as hemlock bark are to be disposed of, the cost of pressing is an unnecessary expenditure ; but if it is desirable to obtain the highest value from the tan, or if the furnaces are not well constructed for burning very wet fuels, it will be profitable to press the tan. Hydraulic presses have been used for this purpose, but those now commonly employed consist of powerful rollers arranged in the same way as those of the myrobalans-crusher (p. 386). The pressure is given by levers loaded with weights or fitted with powerful springs. The liquid which runs from these presses is of little value, as it contains such large quantities of finely divided material that it is almost impossible to filter it, and if run upon the leaches it chokes them and prevents their proper circulation. Much of the cost of pressing is caused by the labour of feeding it to the press, and this may be greatly reduced by the use of mechanical conveyors (p. 390) from the leaches. A tan press is shown in fig. 122.

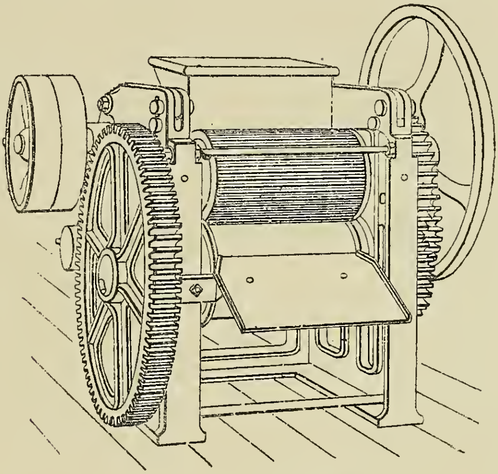

FIG. 122.—Tan Press.

Sewage and other Waste Liquids.—The waste liquors from the different liming, bateing, puering, tanning, washing, and other soaking processes are, without any doubt, the most troublesome of any of the side-products which are obtained in the manufacture of leather. In former times they were simply run into the nearest stream, but nowadays the various sanitary authorities and other similar bodies will only permit comparatively pure waters to be turned into public streams or watercourses.

Various methods of effecting the necessary purification of the waste liquors from tanneries have been proposed at different times, and have been used with varying degrees of success. These methods may be divided into three heads: precipitation, followed by filtration or sedimentation; land-treatment; and bacterial purification.

The first of these depends on the power of certain substances, such as alumina and oxide of iron, to carry down organic matter with them if precipitated in solutions containing it. The method usually consists in adding a sufficient quantity of lime to render the waste liquid slightly alkaline, and then treating it with some crude salt of aluminium or of iron, or *vice versa*. By this means a precipitate of aluminium or iron hydrate is formed, which encloses within itself a considerable proportion of the organic matter of the liquid, and after settling to the bottom of the precipitation-tank is drawn off as "sludge." Various chemicals are sold under fancy names, such as "alumino-ferric," "ferrozone," etc., and have a composition not very dissimilar to that of crude sulphates of iron or alumina. In some cases by-products, such as the acid liquors used in preparing iron articles for "galvanizing," can be used with advantage.

In the case of the waste liquors from a tannery, the use of these chemicals may often be avoided or reduced if sufficient care be taken in regulating the proportion of the various liquids which are to be mixed together and run into the settling-tank. As tanning matter combines with lime and dissolved hide-substance to form a heavy brown insoluble precipitate, it is clear that if care be taken to have rather more waste lime-liquor mixed with the waste tan-liquors than is necessary to throw all the tan out of solution, a very considerable amount of purification of the effluent will have taken place without any cost whatever to the tanner. Hence, if the proportion of waste lime is small in comparison to that of the tanning liquors, an extra addition of lime may be necessary in order to precipitate the tannin.

The precipitation- or settling-tanks are usually square or rectangular vessels or pits, the size of which varies with the quantity of liquid to be treated, but of which the depth rarely exceeds 6 feet. They may be divided into two classes—the "intermittent" and the "continuous." In the former class the tank is filled with the mixed waste liquids, taking care that such a sufficiency of lime is present that the mixture is fairly alkaline to phenolphthalein paper, and is then allowed to rest until the suspended matter has settled down to the bottom of the tank, when the clear, or almost clear, upper liquid is drawn off, the remainder being the "sludge"; some means must also be employed to prevent the passage of scum and floating matters. In the case of the intermittent process it is advisable to have two tanks, one of which is being filled while the other one is settling or being emptied. With the continuous process the liquids are run into the tank in the proportions calculated to give a maximum amount of purification, as described above, but as they enter very slowly the undissolved matter soon settles, and consequently the liquid may be continuously run out at the farther end of the tank. This plan, though it does not yield such good results in the hands of unskilled workmen, is yet useful in many cases, as only one tank is absolutely necessary. It is desirable that in running off the tanks the effluent should be taken as near the surface as possible by means of a hinged pipe attached to a float or some equivalent device, and care is required, as the tank gets low, to avoid the escape of any of the sludge.

For continuous settling the tanks are usually long and somewhat shallow rectangular ponds, into which the previously well-mixed precipitating liquid flows through a wooden trough fixed across one end and as long as the breadth of the tank, and perforated with holes to allow the uniform and quiet influx of the liquid, which finally escapes by a similar trough crossing the opposite end of the tank. In front of the exit-trough a "scum board" must be placed, which is a simple plank dipping slightly below the surface of the liquid, so as to prevent any oil, scum, or other floating matter from passing out of the tank along with the clear effluent. Whether the intermittent or continuous system is employed, the effluent should in most cases be afterwards passed through a bacterial filter-bed, or treated by land filtration, before it is allowed to flow into a stream or river. Tannery effluents are usually received into sewers without further treatment than mixing and settling to remove solid matter, and many authorities are satisfied with the removal of merely such coarse suspended matters as might choke the sewers. Where continuous precipitation-tanks are used they must be emptied at frequent intervals, and the sludge run on to cinder-filters to part with most of its water. These filters are conveniently placed at a lower level than the settling-tanks, and it is generally necessary to return the effluent from them for further precipitation and settling. Several types of continuous settling-tank with upward flow have been devised by Mr Candy and others, which are very suitable for use where space is limited, but otherwise less costly constructions are often sufficient. Apart from the question of obtaining an effluent sufficiently good to satisfy the sanitary authority, the treatment of the sludge is one of the greatest difficulties in the purification of effluents. It is usually very bulky, easily putrescible, and therefore difficult to dry; it is of little value for manure; and if allowed to remain long wet, its smell is very offensive. Chloride of lime is probably the best disinfectant.

It has been mentioned that in most cases the liquid, and in every case the sludge, must be freed from solid undissolved matter by filtration. This may take place through open filters or through filter-presses. The open filters generally consist of a pit with an exit at the bottom for the filtered liquid. This pit is filled with either stones and sand, with clinker, ashes, or coke. Most tanners use clinker and ashes, as they do not cost anything; and the material should be so arranged that while the lowest layers are very coarse, the surface of the filter-bed should be of the finest material. As soon as this has become covered with so thick a layer of solid matter that the filtration proceeds too slowly, the top surface of the filter may be removed with a rake (taking care to remove as little of the ashes or sand as possible), and burnt, or dried and used as manure. In some cases filter-presses are used which are composed of grooved or perforated plates with cloths between them through which the liquid is forced by pressure. The solid matter remains behind in the form of a comparatively dry "cake." The filter-cake, dried if desired, is sold as manure, for which it is in many ways very suitable, though its value as a fertiliser is not great. Although they work much more rapidly than do the open filters, the cloths so soon become rotten and have to be replaced, that the open ash-filter is on the whole the most convenient for the tanner's use. It will be readily understood that apparatus of this kind, though very efficient on a small scale, is quite out of the question when many thousand gallons of liquid have to be filtered daily, and so can only be effectively applied to "sludge."

No system of chemical precipitation has as yet proved entirely satisfactory. Undoubtedly a great deal of purification is effected by this means, but in most cases the "purified" liquid is still too impure to be turned into a stream, though for various reasons this is often permitted by the authorities.

A great advance was made in the purification of effluents when manufacturers were compelled by law to allow the effluent from the precipitation-tank to filter through land set apart for that purpose. In this case certain hardy cereals were sown on the land, which was watered as often as possible with the effluent. This latter, after soaking through the land, was drained off into the nearest stream. Although in many ways this treatment was satisfactory, it had the disadvantage of being very expensive, especially in the neighbourhood of large towns where the price of land is high, and, in addition to this, the conditions necessary for success were far from being correctly understood, so that the land often became " sewage-sick " or waterlogged, and ceased either to produce crops or to purify the effluent. It was not until the researches of bacteriologists proved that the purification by land-filtration was mainly due to the bacteria in the soil that any really satisfactory solution of the problem could be found, but the question has now been to a considerable extent simplified by the introduction of " bacterial treatment."

Bacteria, considered from the point of view of their action on organic matter, are often classified as " anaerobic " and " aerobic," though many species are capable of existing under both conditions (cp. *L.I.L.B.*, section xxiv.). The anaerobic bacteria thrive only in the absence of air, and their chemical action consists in breaking down the organic matter on which they feed into simpler, and generally more soluble, forms by processes which do not involve oxidation. The aerobic bacteria, on the other hand, require air or oxygen for their existence, and produce changes which are usually of a less complex character, but result in the complete oxidation and conversion of the organic matter to simple compounds, such as nitrates and carbonic acid, which are perfectly harmless and inoffensive. The two classes therefore are to a large extent complementary to each other, the anaerobic bacteria converting the animal or vegetable substances into more soluble and simple compounds which are adapted to the needs of the aerobic, which complete the destruction of the organic matter.

In harmony with what has just been said, bacterial treatment of sewage is of two kinds, each of which may be used alone or in conjunction with a preliminary precipitation-process, but which are generally best used successively. The oldest form of bacterial purification depends mainly on the action of anaerobic bacteria, and is known as the " septic tank." This originally consisted of a tank sometimes filled with small pieces of coke, but generally containing the liquid only, and which was tightly closed to prevent access of air and escape of foul gases. It has, however, been found that if deep tanks (6 to 10 feet) are employed, they soon become in continuous use so covered with scum and floating matter as effectually to prevent access of air and light or any serious escape of smell. The liquid to be purified is allowed to flow very slowly through a tank or series of tanks of this description, entering about a foot below the surface through a distributing trough at one end and flowing out similarly at the other, at such a rate as to change the contents of the tank about once in twenty-four hours ; and when the tank is in working order, the liquid is much purified by the process, and most of the solid organic matter has become liquefied and disappears. It not unfrequently happens, especially where the septic-tank treatment is not very prolonged, that the liquid which escapes has a stronger and more offensive odour than it had on entering the tank. It is nevertheless really purer than before, the increased smell being due to the volatile products of the partially decomposed organic matter, and by passing the liquid through an open coke-filter the smell will be effectually removed. In all cases it must be borne in mind that as septic tanks and bacterial filters depend for their efficiency on the organisms they contain, time must be allowed for these to develop and accumulate before good results are obtained ; and for this about six weeks' use is generally necessary, after which they will continue to act for an indefinite period until they become choked by sand and inorganic matter.

It must not be supposed that the action in the septic tank is wholly anaerobic ; and with weak sewage, most of the organic matter may under favourable circumstances be converted into nitrates and carbonic acid by this means only ; but generally a much more complete purification is effected by the subsequent use of " bacterial filters." These in their simplest form consist of tanks of about 4 feet deep, filled with coke, broken bricks, or clinkers, and fitted with drain pipes at the bottom, by which they can be easily emptied. These tanks, often known as " contact-beds," are filled with the sewage or septic-tank effluent, which is allowed to remain on them two hours, and the tank is then emptied, and allowed a rest of six hours for oxidation and aeration, during which considerable heat is developed, which promotes the bacterial activity. In most cases the sewage requires two such treatments, the last often through a bed with finer coke, in order to be completely freed from putrescible matter. In place of the intermittent process, as applied on the contact-beds, continuous aerobic filtration is often employed, the bed being so constructed as to allow of free admission of air at the bottom and sides, and the liquid to be purified being distributed on the surface by a sprinkler or some similar device, and allowed to trickle through the bed. The continuous process seems likely to supersede the intermittent one, as the beds are not only capable of treating a much larger quantity of sewage in proportion to their area, but are also less liable to choke. About six weeks is required, with either contact-beds or continuous filters, before the material they contain becomes coated with the necessary bacterial layer and they get into full working order. The results as regards the effluent are perfectly satisfactory, and the great difficulty and cost consists in the slow but inevitable choking of the beds, which involves the replacement of the porous material. This is considerably delayed by the use of a settled or precipitated sewage, and in this respect, beside its bacteriological function, the septic tank serves a useful purpose in settling insoluble matter, which is much more cheaply removed from it than from the filter-beds. It will be obvious that ordinary settling-tanks, if deep, fulfil many of the functions of the septic tank, and both lead to the production of a much more uniform liquid from the different effluents which the tanner produces, which is important in the subsequent bacterial purification. A good deal of interesting information on these subjects will be found in a paper by Mr W. H. Harrison on the "Bacteriological Treatment of Sewage."[1]

There are a good many patents in connection with the various methods of sewage purification, and some caution is necessary to avoid their infringement, though of course the general principles of settling and filtration, and the destruction of organic matter by bacterial action, are open to all.

As a general rule the waste liquors from a tanyard or leather dye-works are exceedingly impure. They contain the organic matter (in a state of great putrefaction) from the soaks, bates, and puers; other organic matter, also more or less putrefied, from the tan-pits; the lime liquors, with their large proportion of lime and of dissolved protein, and in addition the various dyes and other chemicals which may have been used in the conversion of the raw hide into the finished leather; and hence their efficient purification has presented difficulties which do not occur in most other trades.

The different waste liquids are best run into a capacious tank, and, after being thoroughly mixed up together, are allowed to settle for some hours. By this means the greater part of the tanning matter will combine with the lime also present to form a heavy, brown insoluble substance; some of the dye and other organic matter will become entangled in this, and thus be removed from the liquid. The clear liquid is next run off into a bacterial filter (preferably a septic tank, followed by an open coke-filter),

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[1] *Journ. Soc. Chem. Ind.*, 1900, p. 511.

and then into the nearest stream. If the tannery is near to a town, and the corporation sewers can be utilised, it is probable that a filter made of spent tan may be substituted, as this material will not only remove all excess of lime from the liquid, but will also fix much of the colouring matter (Koenig). The tan, after being used for this purpose, contains so much lime in its pores that it is said to be useful as manure.

In tanneries where large quantities of disinfectants, such as mercuric chloride, carbolic acid, etc., are used, it is necessary that the mixed liquids shall contain so much lime as to make them distinctly alkaline. In this way most of the disinfectants will be either precipitated or rendered inactive. Where arsenic is used in the limes it may be advisable to add a little ferrous sulphate (green vitriol or copperas) in order that the arsenic may form an insoluble compound with the iron, and so be removed along with the sludge. The ink produced by the action of the iron salt on the tan liquors will be completely removed by the bacterial filter.

The problem of the utilisation of leather-scrap, shavings, moisings, and fluffing dust is a very difficult one. Although leather contains considerable quantities of nitrogen, its value as a manure is negligible, since it takes at least years to decay in the soil or to produce any useful effect. It is easily pulverised by scalding with steam or boiling water, drying, and grinding, but even the fine powder is almost imperishable. Probably better results would be obtained by treating it with strong, and if possible hot, sulphuric acid and incorporating it in superphosphate mixtures, but, judging by the time it takes for solution in Kjeldahling, even this would not be very effective. It would also be decomposed by heat and alkalies, but in this case it would be difficult to prevent the escape of the ammonia formed. Probably the best treatment is destructive distillation and recovery of ammonia from the escaping gases. In some experiments on condemned army boots 513 lb. of ammonium sulphate was recovered from a ton. The residual charcoal would also have decolorising and deodorising power, and there would be a good deal of combustible gas.

Pulped leather has been used in mixture with vegetable fibre for making leather-board, but apparently the less proportion of leather the better the result. It seems curious, however, that some satisfactory way cannot be found of compacting pulped leather into stiffeners, heels, and various articles of that sort for shoe manufacture.

A suggestion has been patented by S. Brough (1910) for the use of leather cut into small pieces, in conjunction with asphalt, bitumen, and limestone, for the making of more resilient roads, but, even if successful, the quantity available would not go far on the roads of the country. Possibly, however, a coating for concrete floors might be made on the same principle, which would render them warmer and more comfortable. Grease should be recovered from any leather containing it (pp. 559, 379), and means are described for stripping chrome leather on p. 572.[1]

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[1] Compare M. C. Lamb, *Journ. Soc. Chem. Ind.*, 1917, p. 986, and his patent for stripping with oxalic acid, E.P. 132,864.

CHAPTER XXXII

CONCLUSION

It may be well in concluding this book to sum up shortly the most important of the advances which have been made since the publication of the first edition of 1903, some of which have been already discussed, while others are here alluded to for the first time in these pages; and perhaps also to allow myself a few words of suggestion as to the opportunities for progress in the near future.[1]

Among the most important of the practical gains which are also of scientific importance may be mentioned Dr Stiasny's discovery[2] of a new class of synthetic tanning matters, the syntans, which can be produced so cheaply as to have already found extensive use in the tannery. From the scientific side these tans, of comparatively simple constitution, offer an opportunity for the investigation of the relation of constitution to tanning effect which may throw much light not only on the nature of the vegetable tanning process, but on the causes of the quality we call astringency.

Less important are the discoveries[3] of the effect of hydroxy-acids such as tartaric, which by forming complex ions with chromium renders possible the removal of chrome from chrome-tanned leather by Rochelle salt (sodium-potassium tartrate), and explains the effect of some of the products which occasionally occur in chrome liquors reduced by organic matter, producing purple liquors which will not tan; and the production of concentrated chrome liquors by the direct reduction of strong solutions of sodium bichromate with sulphurous acid.[4]

An interesting new departure is also the vacuum tanning process of Mr Nance. All previous attempts to introduce tan into leather by the same use of vacuum as is so successful in creasoting timber (and there were many) had failed because the

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[1] A portion of this chapter is taken from a lecture given by the writer to the Conference of the Leather Trade Federations at the Leathersellers' Hall, 17th November 1920.

[2] Ger. Pat. 262558, 1911.

[3] *Journ. Soc. Chem. Ind.*, 1916, p. 230.

[4] *Journ. Roy. Soc. of Arts*, 66, 1918, pp. 747, 776.

pores of the hide are filled with incompressible water instead of with air, and it was not until Nance used a vacuum so high that the water actually boiled in the pores of the hide at a temperature of only 70° or 80° F. that the water could be expelled and the entry of tan-liquor made possible.

A new departure in drum-tannages is the use of viscous colloids, such as tragasol[1] and starch paste,[2] as vehicles for the tanning extract, which allow it to be used in concentrated form without hardening the surface or drawing the grain, and probably themselves contribute to filling the leather.

Of more scientific interest, though perhaps of less immediate commercial importance, are Professor Meunier's investigations[3] on tannage with various chemical substances, and especially with quinone, which gives one of the most perfect and resistant leathers known, though its price precludes it at present from any extended use. Quinone is a derivative of benzol, a ring of six carbon atoms, to each carbon of which, in benzol itself, an atom of hydrogen is attached. In phenol (ordinary carbolic acid) the place of one of these hydrogens is taken by an OH or hydroxyl group, and the substitution of a second OH gives, as might be expected, three di-hydroxy-phenols, alike in composition, but differing in properties, and in the place of the second OH on the ring. Taking the OH of common phenol as in the noon position, the two o'clock position gives catechol, the source of all the catechol tannins; the four o'clock is resorcin, present in the dyestuff orcin; and the six o'clock is hydroquinone, the common photographic developer. If hydroquinone be oxidised by exposure to the air or otherwise, the H's of the two hydroxyls combine with the O to form water, and the spare links of the deserted O's join hands across the ring and form quinone. Such a structure is naturally little stable, and in presence of hydrogen easily reverts to hydroquinone. In a 1 per cent. solution of quinone, pelt becomes first rose-coloured, then violet, and finally brown, and is converted into a soft tough leather which will stand boiling and washing with soap or even with dilute acids or alkalies, and which dyes readily with acid, basic, and mordant dyes. Meunier found hydroquinone in the used liquor, thus proving that the skin had not merely combined with quinone, but with oxygen. A similar tannage can also be produced by hydroquinone, but more slowly, and only in presence of air. The oxidation of the hide-substance is of

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[1] Gum Tragasol Supply Co. Ltd., Hooton, near Chester.

[2] A. Turnbull and B. Carmichael, Eng. Pat. 101470, 1917.

[3] *Coll.*, 7, 1908, p. 195. *Ibid.*, 8, 1909, pp. 58, 319. Ger. Pat. 206957, 1909.

some theoretical importance. Meunier concludes that the quinone combines with the amino-groups of the skin, to which apparently acids and vegetable tannins also attach themselves.

Meunier pursued his researches with other phenols and phenol derivatives, such as pyrogallol and gallic acid, and found that most of them would tan if exposed to the oxidising action of the air, and still more rapidly when in a slightly alkaline condition, which promotes oxidation. Gallic acid with access of air rendered gelatine insoluble in three days, while gallotannic acid failed to do so in twenty-six days in a closed vessel, but rapidly did so when air was admitted. This seems to show that air has some function in tannage which has not been generally recognised, though whether the skin or the tannin, or both, must be oxidised is not yet clear. It may, however, be pointed out that if tannin will not tan gelatine *in vacuo* it will certainly tan skin, and the reason may possibly be that while the tannin permeates the hide and penetrates the extremely fine fibres, it is not able to penetrate gelatine in the mass, but only tans the surface, while the insolubilisation of the interior is due to the oxidation of the gallic acid which is always present in commercial tannin or is formed by its decomposition. In experiments on the diffusion of tannins in gelatine jelly it has been found that this is apparently the case. Meunier's statement that gallic acid tans more rapidly in alkaline solution is noteworthy, and shows that its mode of action is radically different from that of the tannins, which will only tan in an acid medium. The gallic acid is, however, probably absorbed as an acid, though it only exerts its tanning effect when oxidised. The work throws an important and rather unexpected sidelight on the vexed question of the value of the phenolic non-tans, such as gallic acid, which are present in all tanning materials. Though partially absorbed by hide-powder in the ordinary analytical process, they certainly do not tan, and Wilson[1] has shown that they can be removed from it by washing, but it is clear that if exposed to the air in drying they will become fixed by oxidation, producing an actual tanning, and adding to the weight and solidity of the leather. These facts will have to be considered in any revision of the analytical method. The ideal analytical method of the future should give much more detailed information as to the constituents of the tan, but will consequently cost more in execution, for which users will have to pay, and the present process, imperfect as it avowedly is, has become of such commercial importance that no changes, even for the better, can be lightly undertaken.

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[1] *Journ. Amer. Leather Chem. Assoc.*, 1920, p. 295.

Meunier,[1] following up the clue of oxidation, next experimented with such well-known oxidising agents as chlorine, bromine, and iodine, all of which precipitate gelatine from its solutions as insoluble compounds, and found that all were capable of converting skin into leather. Bromine, especially, in dilute solution, and with addition of salt to prevent undue swelling from the hydrobromic acid produced, speedily tanned the skin, which after washing with water, or more rapidly with a solution of sodium bisulphite to remove the surplus bromine, formed a white, supple, and fine-grained leather of considerable toughness and resistance even to hot water, and which contained about 0·9 per cent. of bromine on the dry gelatine. Equally good and very similar results were obtained by the use of sodium hypobromite, formed by adding soda to the bromine solution till its yellow colour was just discharged, and in this case salt was not necessary, though the washing with water and bisulphite could not be omitted.

As bromine is too expensive for ordinary use it seemed desirable to experiment with the much cheaper chlorine, but gaseous chlorine or chlorine-water broke up and dissolved the gelatine before rendering it insoluble. Much better results were obtained with sodium hypochlorite (*eau de javelle*) and with bleaching powder, but more care was required than with bromine, and it was necessary to work at temperatures at or below 10° C. (50° F.), which would be difficult in practice in summer, but Meunier suggests the use of the process for the temporary preservation of skins in place of pickling, or for their preparation for other tannages, and this might be practicable where very cold well-water was available. Ordinary "hypo" might no doubt be substituted for bisulphite for washing out the excess of hypochlorite.

In all these cases the tannage appears to be wholly chemical, and no solid body which could coat the fibres is produced, so that neither Knapp's theory of coating the fibres nor the more modern ideas of adsorption can well apply. They give some colour, however, to a theory of Fahrion's as to the necessity of oxidation of the fibre itself.

To complete his investigations on the theory of tannage, Meunier next experimented with a purely physical tannage by dehydration and isolation of the fibres on the principle of Knapp's alcohol leather,[2] but instead of alcohol he employed solutions of potassium carbonate, which have a very high osmotic pressure

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[1] "Le tannage au brome," *Coll.*, 10, 1911, pp. 289, 373.

[2] *Coll.*, 11, 1912, pp. 54, 420.

and affinity for water. Placed in strong solutions, up to 80 per cent., water flowed freely from the skin under the osmotic pressure of the solution, which seemed scarcely to penetrate it, and in a few hours left it in a state when after "putting out" with the sleeker, or even wiping with a cloth, it could be dried rapidly in the air, and after staking formed a soft white leather which was permanent so long as dry, but returned rapidly to pelt when soaked in water. As very little potassium carbonate is actually absorbed, there is a commercial possibility of using this process as a substitute for pickling.

Another interesting set of experiments were made by repeating similar experiments in duplicate with potassium carbonate, and adding to one set 3 c.c. per litre of commercial formaldehyde solution. Where the potassium carbonate solutions were of less than 10 per cent. the leather of both series dried hard and horny, and more concentrated ones were necessary for good results. In each series the skin was equally leathered, but while those with the carbonate alone returned to pelt on soaking, those with formaldehyde when re-dried were as soft as before. Meunier concludes from this that the function of the sodium carbonate in the Payne and Pullman process is merely that of dehydration, and not that of an alkali. I am not myself quite convinced on this point, since their patent specifies only 1·9 to 2·8 per cent. of sodium carbonate, which is less dehydrating than the potassium salt, and in Meunier's experiments would be quite insufficient to produce a soft leather, while I can say from my own observation that Pullman's skins were perfectly leathered in the drum. It is, however, certain that satisfactory formaldehyde leather can be produced in the presence of other salts which are not alkalien. Meunier's opinion of formaldehyde as a tanning agent is not a very high one. He states that it slowly evaporates on exposure to air, leaving the leather hard and brittle, and that it can be removed by continued treatment with hot water, being in that respect very inferior to his quinone tannage. We have found at Leeds that formaldehyde can be quantitatively recovered from leather by hydrochloric acid so weak as decinormal.

In connection with what has been said on new tannages, it is perhaps worth while to mention the accidental discovery of one in which I had a part. I had noticed in the laboratory the powerful dehydrating effect of saturated solutions of ammonium sulphate, which easily produce a white leather like Meunier's, and I communicated this to Mr Seymour-Jones, thinking it might be useful in some cases where the use of acid in pickling is objectionable. He tried it on a practical scale, but used commercial ammonium sulphate, which contains traces of tarry phenolic products, and found to his disappointment that the leather was permanent, and would not return to pelt. It is quite possible that by the choice of suitable tar-products a leather might might be made of commercial value.

Leaving Professor Meunier, I must turn to the work of some other chemists. It was noticed by Lüppo-Cramer[1] that colloidal silver peroxide precipitated in the gelatine film of photographic plates rendered it insoluble in hot water, and that it had the same effect on gum-arabic and starch. More recently Dr Erich A. Sommerhoff discovered that colloidal precipitates, such as hydroxides, sulphides, phosphates and silicates of the heavy metals, when drummed into pelt, rapidly produced complete tannage, and, what is much more surprising, that ultramarine, a fine and quite insoluble powder, had a rapid tanning effect. It has long been known that leather could be formed by the precipitation of such bodies in or on the fibre : Phosphate leathers have been commercially produced, and the " pyrotan " process owes at least part of its efficacy to a similar effect. Leathers have also been made, not only by chrome and alumina, but by other metals producing basic salts hydrolysed by the skin ; and the two-bath chrome leather owes its superior softness to that of basic tannage to the sulphur deposited on the fibre. Probably almost any colloidal precipitate is capable of producing leather.

Instances of this sort might be multiplied almost *ad infinitum*, but enough has been said to show that no single theory of tannage can embrace all possible cases, and that in most commercial processes more than one of these actions is involved.

The investigations of H. R. Procter and his collaborators, amplified by many others, and especially by Dr J. Loeb, have been sufficiently described in other parts of this book and need not be discussed here, but it has much emphasised the importance of extended investigation of the region lying between ordinary alkalinity and acidity, roughly that between the reactions of phenolphthalein and of methyl orange, in leather chemistry, since within it lie the isoelectric points of gelatin and hide-fibre, on the one side of which these bodies act as acids and on the other as bases, and which is therefore the turning point in the reactions involved in tannage (p. 118). It is obvious that this region cannot be investigated by the ordinary methods of titration, since it is mostly a question of the actual hydrion-concentration and " true " acidity, and not of the total con-

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[1] *Coll.*, 7, 1908, p. 24.

centration of unionised acids, and quite different means must therefore be adopted. The most satisfactory of these methods is the electrometric, in which the actual acidity at the moment is determined by the electric potential of a voltaic cell, in which the positive element is a platinum plate saturated with hydrogen, but this method involves an elaborate apparatus and delicate manipulation which is not suited to the ordinary work of the tanners' laboratory. It is therefore of great practical importance that the invention of the "comparator" (App. D) has brought an approximate determination within the range of ordinary laboratory work, and at least made a great forward step in the determination of the swelling power of tanning liquors. Its effect in the control of liming and bating is not likely to be less than that with regard to the actual tanning, since the depleting effect of deliming is dependent on the closeness of the approach to the isoelectric point and the swelling power of limes on the concentration of ionised OH, just as that of liquors is on that of H^+.

While it is still hard to say whether tannage is in the main a "chemical" or a "physical" process, the work of the last twenty years has much emphasised the importance of the study of the colloid state of matter, and especially of the electric charges of the colloid particles on which their chemical action depends, and which usually change in sign at their isoelectric point. We are still in ignorance of the exact position of many of these isoelectric points, and their determination is a necessary work of the future.[1] More information as to the "dispersity" or size of the particles under different conditions of temperature and dilution is also urgently required, and in some important cases, as in that of chrome liquors, we do not yet know with certainty whether we are dealing with molecular or colloidal solutions.

The valuable work of J. T. Wood on the bacteriology of bates, puers, and drenches was largely completed before the first edition, but since that time he has added largely to our knowledge of the enzymes concerned in these processes, and the trypsin bates have increasingly taken the place of those containing active bacteria; and it is not likely that these will again come into use, though we may have to resort to bacteria for the production of the necessary enzymes (p. 219). The bacteriology and ferments of limes and liquors is however still to a large extent unexplored, and it is to

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[1] The isoelectric point of gelatin is $P_H = 4{\cdot}7$, and that of hide-fibre appears to be practically the same. See E. C. Porter, *J.S.L.T.C.*, 1921, p. 259.

be hoped that the new Research Institute of the Tanners' Federations may be able to throw light on these important subjects.

Mr Seymour-Jones's work on the histology of the animal skin is also a valuable addition to our knowledge, and we can only wish him health and strength to complete his promised book upon the subject.

Since the first edition great improvement has taken place in our analytical control methods, but the primary one of tannin determination has undergone little or no change, and though there seems little hope of superseding the present useful but empirical method, the time is approaching when its revision will be necessary, however difficult it is to make changes in one which has become of so great commercial importance. Mr J. A. Wilson's work has thrown new light on the large amounts of what are not strictly tannins which are absorbed by hide-powder, and without denying their uses to the tanner, it seems desirable that this should be reduced and made more constant, perhaps by a limited washing of the powder with addition of the washings to the non-tannin filtrate. The attempts to prepare a powder of absolutely constant absorptive power have proved largely abortive, and it is a question whether the origin of the trouble does not lie rather in the varying acidity of the liquors than in that of the hide-powder. At the same time it has been shown that a slight acidification of the liquor would greatly simplify the determination of the difficultly soluble tans by rendering them readily filterable, though at the same time probably increasing their amount.

APPENDICES

APPENDIX A

THE DECIMAL SYSTEM

The metrical system of weights and measures and the Centigrade thermometer scale have been generally used throughout the book as more international and scientific than the complicated systems still unfortunately in use in this country. Its much greater convenience in calculation, and the fact that it must ultimately come into use throughout the civilised world, and is already the only system in use in scientific laboratories, also make its comprehension imperative. It has the advantage of being based on a single measure of length, the meter, from which all other measures of area and capacity are derived, so that instead of having to learn separate tables for each of these, it is easy to pass by a mental calculation of squaring or cubing from one set of dimensions to another. Thus the cubic decimeter is the liter, and a cubic meter is 1000 liters, and the liter of water weighs a kilogram, and the cubic meter a metrical ton or 2204·6 English lbs., and if we know the specific gravity of a body, its weight in kilograms is at once apparent. Thus a stone of Sp. Gr. 3·0 and 1 meter cube is at once seen to weigh 3 metrical tons, and for most aqueous liquids the weight does not vary seriously from 1 kilo for each liter.

The following table gives the figures required for reduction from the English to the metrical system, or *vice versa*:—

1 meter = 39·37 inches.
1 millimeter = 0·003937 inch.
1 liter = 0·2202 gallon.
1 cub. cm. water = 15·432 grains.
1 cub. meter = 35·317 cub. ft.
1 foot = 0·3048 meter.
1 inch = 25·34 millimeters.
1 gallon = 4·541 liters.
1 grain = 64·8 milligrams.
1000 cub. ft. = 26·314 cub. meters.

Actual reduction is, however, generally unnecessary if the question be treated as one of proportion. Thus a solution of 1 gram per liter is of the same strength as one of 1 lb. per 100 gallons (1000 lb.), and very approximately, as one of 1 oz. avoirdupois per cubic foot (1 cubic foot weighs 9971 oz.). In the case of pits, it is often simplest to measure them directly with a meter rule; length, breadth, and depth, measured in decimeters and multiplied together, giving the contents in liters, and, in the case of water, the weight in kilograms. The capacity of a rectangular tank is length × breadth × depth, that of a cylindrical one is (half-diameter)^2 × depth × 3·1416, or approximately by $3\frac{1}{7}$: the Imperial gallon is 277·274 cubic inches, and that of water weighs exactly 10 lb. at 62° Fahr. The American gallon is the old English wine gallon, and contains only 231 cubic inches.[1]

The Centigrade or Celsius thermometer divides the difference between the freezing and the boiling points of water into 100°. The following table gives the points at which its scale agrees without fractions with that of Fahrenheit :—

COMPARISON OF CENTIGRADE AND FAHRENHEIT DEGREES

°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.	°C.	°F.
−20	− 4	0	32	20	68	40	104	60	140	80	176	100	212
−15	+ 5	5	41	25	77	45	113	65	149	85	185	105	221
−10	14	10	50	30	86	50	122	70	158	90	104	110	230
− 5	23	15	59	35	95	55	131	75	167	95	203	115	239

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[1] The avoirdupois pound is 7000 grains and the ounce $437\frac{1}{2}$ grains. The troy and apothecaries' pound is of 5760 grains, and the ounce (in which all precious metals are weighed) is 480 grains, but the "fluid ounce" of water is only $437\frac{1}{2}$ grains. In chemistry the "Mohr's liter" (1 kilo of water at 15° C.) is generally used in place of the true liter of 1 kilo at 4° C.

APPENDIX B

ORIGINAL PAPERS ON THE GELATINE EQUILIBRIUM

As most readers dislike (and shirk) mathematics, and it is yet impossible thoroughly to understand a mathematical subject without it, it has seemed best to print two of the most important original papers in full, rather than burden the text with a long mathematical explanation. The selection has been made on several grounds. The first paper was originally published in German, and though it has since appeared in English in the *J.A.L.C.A.*, there are many readers to whom it is not readily accessible. It contains a mass of experimental work, much of which has been utilised in subsequent papers, and for a full understanding of any question it is important to know something of its historical development ; and it is indeed the want of this which leads many unscientific people to complain of the changeableness of scientific views, when, with more knowledge, they would realise that the newer view is simply the logical and necessary outcome of the older in the light of wider knowledge. Though this first paper left much of the problem unsolved, it is interesting to its writer to see how much of the later solution is suggested ; and the final answer was only rendered possible by the important papers of Professor Donnan on " membrane equilibria, " which were published in the same year. A curious proof of the scientific foundation of the theory is found in the determinations of " acid fixed " which are given in Tables III. and IV. and shown in fig. 123, and which produced a peculiar curve which at the time seemed inexplicable. The explanation could not be given till 1914, when an equation to the curve was published in the *Trans. of the Chemical Society*, p. 325, and its exact parallelism with the experimental results was most striking. The rather important paper (*Trans. Chem. Soc.*, p. 313) in which this appeared is not here reprinted, as it is pretty readily accessible, and, although it marked a great advance at the time, the theory has been considerably amplified and perfected in the paper of 1916 by Procter and Wilson, which is given.

A list of some of the more important papers on the acid-gelatine equilibrium are given :—

H. R. Procter, "Action of Acids and Salt-solutions on Gelatine," *Journ. Amer. Leather Chem. Assoc.*, **6**, 1911, p. 270.

H. R. Procter, "Equilibrium of Dilute Hydrochloric Acid and Gelatine," *Journ. Chem. Soc.*, **105**, 1914, 313.

Procter and Wilson, "Acid-gelatine Equilibrium," *Journ. Chem. Soc.*, **109**, 1916, 307.

Procter and Wilson, "The Swelling of Colloid Jellies," *Journ. Amer. Leather Chem. Assoc.*, **11**, 1916, 339.

J. A. and W. H. Wilson, "Colloidal Phenomena and the Adsorption Formula," *Journ. Amer. Chem. Soc.*, **40**, 1918, 886.

And other papers, particularly those of J. Loeb in *Journ. Gen. Physiology*, 1918–1921.

PART I.—ON THE ACTION OF DILUTE ACIDS AND SALT-SOLUTIONS UPON GELATINE[1]

By Henry R. Procter

The investigation which forms the subject of the following paper was begun in 1897, and much of the experimental work was done in 1898 in conjunction with Mr Richard Paget, who, it was hoped, would share in the authorship of the paper. Circumstances, however, prevented its completion in co-operation, and the work has been carried on at intervals, with various assistance, up to the present time; and although there remain many points still unsolved, it seems desirable, in consideration of the present interest in colloid questions, no longer to delay the publication of what is already completed.

The investigation was originally undertaken in the hope that the study of comparatively simple cases of colloidal swelling and contraction might throw some light on the complicated phenomena of the tanning process, and especially on the very curious results of the treatment with acid and salt known as "pickling," and on the mineral tanning processes in which acids and salts are employed; but as it proceeded it became obvious that much wider and more important scientific issues were involved, which included the whole theory of colloid swelling.

The pickling process consists in principle in treatment of the skin with a very dilute bath of sulphuric acid, in which the connective-tissue fibres are strongly swollen; and subsequent immersion in a concentrated solution of common salt, in which not merely the swelling disappears, but the fibres become greatly dehydrated, and the skin converted into a kind of leather. As

[1] This article was published in German in *Kolloidchemische Beihefte*, Bd. II., Heft 6–7, 1911. It also appeared in the *J.A.L.C.A.*, 6, 1911, p. 270.

even saturated solution of common salt has no dehydrating effect without the preliminary acid treatment, the effect is at first sight striking and unaccountable.

The swelling action is complicated in skin by its anatomical structure, which allows it to absorb liquids not merely by colloidal swelling, but capillarily in the interstices between the fibres, and it was obvious that no quantitative study could be made unless means were devised to separate the two effects. Fortunately, however, gelatine behaves in a manner at least qualitatively identical with hide-fibre, and the very close chemical relationship between the two justifies the assumption that the same chemical affinities are involved, while from the absence of structure capillary absorption is excluded. Comparative experiment confirmed this anticipated identity of behaviour ; and as the experiments were only intended as a preliminary investigation, ordinary commercial thin sheet gelatine was selected as a material. For the same reason, and to avoid complicating the work, slight variations of laboratory temperature, and other secondary disturbing causes such as adhering moisture, were neglected, and a method of experiment adopted which was capable of comparatively rapid execution. Sheets of thin French gelatine of the purest kind were cut, air-dry, to portions of about 1 gram in weight, and soaked in the requisite solutions, their gain in weight determined after draining as far as possible from adhering moisture, and both the gelatine and the residual solution analysed as regards acid and salt, and the whole calculated to ash-free gelatine dried at 110°, and to milligram-molecules per gram. The air-dry gelatine in the earlier experiments contained 16·07 per cent. of moisture, which, as it was kept in a stoppered bottle, was practically constant ; and 1·19 per cent. of ash consisting mainly of lime with traces of sulphites and phosphates. It was, no doubt, a bone-gelatine. For all the earlier experimental work the same sample of gelatine was used, but for some later series of determinations other gelatines were employed of the same character but not actually of the same parcel. This may account for some variations between different series of experiments, while any single series gave as a rule very consistent curves.

The Swelling of Gelatine in Water

The extent to which a gelatine will swell in cold water at a given temperature is to a great extent a specific quality of the particular sample, influenced by the proportion of partially hydrolysed gelatine-products which are always present in the commercial article. These indeed cannot wholly be avoided, since they are formed to some extent whenever the gelatine jelly is heated so as to melt it, and they are unquestionably the main cause of those variations in character which have been attributed to what has been called the "*Vorgeschichte*" (previous history) of the jelly. Traces of soluble electrolytes also affect it osmotically, and perhaps chemically. That gelatine and other gelatinising substances do not swell to infinity and become colloid solutions like gum and dextrine is due to the solid but elastic structure which is formed at setting, the cohesion of which finally balances the attraction of the gelatine for water. Under these circumstances it seemed not improbable that the swelling maximum of any given jelly would be influenced by the volume of its structure at the moment of setting; and this is proved to be the case by the following experiment.

Solutions containing approximately 5, 10, and 20 per cent. of air-dried gelatine were cast in glass tubes on wire spirals for convenience of handling, and were then dried for some days in a current of dry air, weighed, and allowed to soak in water at laboratory temperature, and weighed at intervals. Taking the weight of actual dry gelatine as unity, the amounts of water absorbed were as follows :—

TABLE I.—ABSORPTION OF WATER BY GELATINE

	5 per cent.	10 per cent.	20 per cent.
Dried in air . . .	0·1	0·1	0·2
After soaking 24 hours .	8·4	4·3	3·7
After soaking 72 hours .	11·7	6·0	5·1
After soaking 96 hours .	12·6	6·5	5·4
After soaking 120 hours .	13·2	6·9	5·5
After soaking 144 hours .	13·6	7·2	5·7
After soaking 168 hours .	14·6	7·7	5·8
In original jelly . .	23·2	11·1	5·0

As will be seen from the figures, the original setting volume has considerable influence on the maximum swelling, but is evidently not the sole determining cause.

Action of Alcohol on Gelatine Jelly

It is well known that the swelling of gelatine jelly can be reduced by treatment with alcoholic solutions, and with absolute alcohol it becomes a hard and apparently dry mass. As there is no reason to suppose any chemical action of alcohol on gelatine, which on soaking in water returns to its original jelly-condition, the case seems a favourable one for the study of the effect of purely physical forces on jellies. Gelatine is practically quite insoluble in cold alcohol either pure or dilute, and conversely, even quite weak jellies are semi-permeable to alcohol in solution. Alcohol placed in a porous cell lined with gelatine, and immersed in water, develops a considerable osmotic pressure, and masses of gelatine jelly dehydrated by alcohol absorb scarcely any of the latter.

In order to get some idea of the effect of alcohol upon swelling, weighed portions of air-dried thin sheet gelatine were immersed in a series of mixtures of alcohol and water for twenty-four hours, and again for twenty-four hours in renewed portions of the same solutions. This length of time had been found sufficient in previous experiments to establish practical equilibrium. The portions were then drained and weighed to determine the swelling, the gravity of residual alcohol taken, and its percentage calculated by the ordinary tables, and the pieces dissolved in hot water, and distilled to a volume of 25 c.c. of distillate, of which the gravity was taken to determine alcohol in the gelatine. Only in the case of the 100 per cent. alcohol did the gravity of the distillate fall so low as 0·999, and in this case only to 0·9979, so that any alcohol found may very well have been that merely adhering to the surface of the gelatine, and more exact methods of experiment must be adopted before conclusive evidence of any solubility of alcohol in gelatine jelly can be obtained, though it seems possible that when the gelatine is nearly dehydrated, some alcohol is absorbed.

A second series of experiments were also made in a similar way, in which the gelatine was swollen in water for twenty-four hours before treatment with the alcoholic solutions. The results, which are given below, are almost precisely similar to those of the first series, except that in the 90 per cent. and 100 per cent. alcohol complete equilibrium does not appear to have been reached. No evidence of penetration of the alcohol into the jelly was obtained, the gravities of the distillate ranging from 0·9996 to 1·000. The equilibrium appears to be completely reversible.

Table II. gives the weight of swollen gelatine obtained from 1 gram of dry. It will be observed that the curve is quite a regular one. The weight of the gelatine from absolute alcohol is slightly less than its weight air-dried.

It is of course impossible to calculate theoretically the osmotic pressures of alcohol in such concentrated solutions as were here used, but the curve is such as would be expected from osmotic

TABLE II.—ACTION OF MIXTURES OF ALCOHOL AND WATER

Original Mixture.		Gelatine Air-dry.		Gelatine first swollen.	
"Absolute". Alcohol.	Water.	Per cent. Alcohol in solution after soaking.	Wt. of 1 grm. Dry Gelatine after soaking.	Per cent. Alcohol in solution after soaking.	Wt. of 1 grm. Dry Gelatine after soaking.
c.c.	c.c.		grm.		grm.
100	0	99·04	1·20	92·63	1·84
90	10	84·08	1·36	81·76	1·80
80	20	73·30	1·50	70·64	1·60
70	30	..	..	60·88	1·68
60	40	51·56	1·70	48·73	1·96
50	50	43·04	2·24	39·80	2·36
40	60	33·22	2·86	30·84	2·52
30	70	24·46	3·14	22·77	3·06
20	80	16·20	3·72	15·17	4·42
10	90	7·93	5·72	7·42	5·96
0	100	0·00	7·23	0·00	7·23

pressure acting on a material with a certain elastic rigidity of its own ; and there seems no reason to invoke other forces. Probably if the osmotic pressures of the alcoholic solutions were independently determined, such experiments might furnish a means to calculate the elasticity of the jelly. Neglecting any small attraction of the alcohol for the gelatine, the equilibrium is probably

$$\left.\begin{array}{c}\text{Cohesive attraction of jelly}\\ + \\ \text{Attraction of alcohol for water}\end{array}\right\}=\text{attraction of gelatine for water.}$$

This is of course merely an inverse way of stating the osmotic view, since osmotic pressures are "partial" kinetic pressures, and may be expressed as "minus internal pressures" of the solvent ; just as in a mixture of air and water-vapour at atmospheric pressure the pressure of air in the mixture is lowered by that of the water-vapour, which is equivalent to a minus atmospheric pressure.

Alcohol, though it precipitates hot gelatine solutions when added in large quantity, can be mixed in moderate proportions without causing separation, and the mass sets to an apparently homogeneous jelly, which, if alcohol is insoluble in jelly, must really consist of alcohol-water solution of such concentration as corresponds to the equilibrium just discussed, enclosed as an emulsion in a jelly medium. Such an emulsion should swell more in water than a plain jelly, since not only will the jelly absorb all the water necessary for its maximum swelling, but the alcoholic emulsion-globules will become diluted, and exert an outward pressure on the jelly mass. On the other hand, if the action of the alcohol were a chemical one, lessening the absorptive power of the gelatine, the swelling should be reduced whether the alcohol were introduced from without, or were already present in the mixture. Experimentally, it was found that of two somewhat concentrated jellies of equal strength, one made with water alone, and one with a mixture of water and alcohol, the latter swelled much the more, thus confirming the emulsion-character of alcoholic jellies. It is almost certain that such jellies would show microscopically the cellular structure which has been attributed by Bütschli and van Bemmelen to jellies in general.

The Action of Acids on Gelatine

It is well known that gelatigenous fibre is swollen by all dilute acids which are sufficiently ionised, although very feeble acids such as boric, carbonic and sulphydric, have little or no swelling effect, and the same is true of many of the weaker organic acids.

Gelatine is similarly affected. A gelatine which absorbs seven or eight times its weight of pure water may absorb over fifty times its weight of very dilute hydrochloric acid. For the most detailed experimental work hydrochloric acid was chosen, as a highly ionised and typical monobasic acid, which could be easily estimated both acidimetrically and by silver nitrate. A further reason for the selection was that although in the commercial pickling process already mentioned sulphuric acid is used in conjunction with excess of common salt, yet the acid principally active must necessarily be hydrochloric; and as a satisfactory pickling can be produced by this and salt alone, nothing could be gained as regards principle by complicating the equilibrium with the presence of sulphuric acid and sulphates.

The general method of experiment was similar to that which has been already described. Pieces of air-dried sheet gelatine of about 1 gram in weight, of which the content in dry ash-free gelatine was known, were soaked in solutions of acid of known volume and concentration for forty-eight hours, which was found a sufficient time to produce a steady equilibrium. The volume and strength of the residual solution was determined acidimetrically with standard KOH solution and phenolphthalein, the swelling of the jelly was measured by weighing after draining, and it was subsequently melted and the absorbed acid similarly titrated, it having been proved by preliminary experiments that the whole of the acid present could be thus determined, and that no difference in result was caused by melting the gelatine. Any slight variations from this procedure are noted in connection with special series of experiments.

In an early series of experiments it was found that though the whole of the acid present in the jelly was estimated using phenolphthalein as indicator, yet only a portion was determined when methyl orange was used, although to free hydrochloric acid both indicators are equally sensitive. It is therefore clear that in the jelly a portion of acid is combined either chemically or by adsorption, in such a way that it is less ionised as regards H-ions than the remainder which behaves as if merely dissolved in the jelly, and of course varies with the degree of swelling. In order to get rid of the complication thus introduced, it was assumed as a first approximation that the absorbed volume of liquid was of the same concentration as that of the surrounding acid solution, and that the excess which was always found on the titration with phenolphthalein was "fixed" or more closely combined with the gelatine. This "fixed acid" proved to be usually somewhat lower but roughly approximate in quantity to that estimated by phenolphthalein but not by methyl orange, and obviously represents the excess of acid absorbed by the gelatine, though it does not accurately determine what portion is attached to the gelatine and what to the absorbed water, and it will be shown later that the quantity of acid really fixed by the gelatine is greater than that so determined. Still it affords a ready means of comparing the character of the absorption, and as such, is given in the tables.

Table III. represents the results of more than one series of experiments, the Roman numerals of the first column indicating the series. These experiments were made in 1899 and 1900 on one sample of French gelatine, the titrations being done mostly by Mr Paget. Table IV. represents experiments made more recently, with slight variations of method suggested by experience, on another sample of gelatine of a slightly more acid character, and with apparently a greater solid cohesion, as the maximal swelling is in all cases less, though the character of the curves and the position of the maxima in general show good agreement with the earlier results. Especially in the lower concentrations of Table IV. some ambiguity is caused by the acidity of the gelatine, consisting mainly of bisulphites, which amounted to 0·282 mgr.-mols. per gram as indicated by phenolphthalein, but did not affect methyl orange, and of which at least a portion diffused into the outer solution, and affected its molecular acidity as determined by phenolphthalein, but could hardly have much influence on the acid "fixed." Determinations of the strength of the outer solution by methyl orange, which certainly represent the whole of the acid present as HCl, are therefore given, with corresponding calculations of "fixed" acid, and of the acid absorbed in the gelatine as determined by the two indicators.

In reference to this work attention must be drawn to a paper[1] by Dr Wolfgang Ostwald on the swelling of gelatine, in which he gives curves for the swelling of gelatine plates in acids and alkalies of different concentrations. In both cases he shows the existence of a maximum such as has just been described, but he also observed a minimum with very dilute solutions, of which the present writer has found no trace.[2] Ostwald himself ascribes

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[1] Wo. Ostwald, "Ueber den Einfluss von Säuren und Alkalien auf die Quellung der Gelatine," *Archiv für die ges. Physiologie*, Bd. 108. Bonn, 1905.

[2] This minimum has since been found at the isoelectric point $P_H = 4 \cdot 7$, or N/50000, but could not well be detected by the means of titration used. (H. R. P.)

TABLE III.—GELATINE AND HYDROCHLORIC ACID

Series No.	Mgr.-mols. HCl in 1 grm. solution after use (Phenolphth.).	Wt. of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. HCl absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Mgr.-mols. HCl absorbed by 1 grm. Dry Gelatine (Methyl Orange).	Acid "fixed" by 1 grm. Dry Gelatine.	Acid of 1 grm. Dry Gelatine not indicated by Methyl Orange.
	a	*b*	*c*	*d*	*c—ab*	*c—d*
XXVI. 1	0·2692	18·25	5·780	..	0·867	..
XXVI. 2	0·2089	17·72	4·460	..	0·758	..
XXVI. 3	0·1546	18·23	3·613	..	0·795	..
XX. 1	0·1425	21·70	3·798	..	0·706	..
XX. 2	0·1250	21·35	3·400	..	0·731	..
X. 1	0·1066	23·87	3·291	2·413	0·746	0·878
XXVI. 4	0·1009	21·84	3·060	..	0·856	..
X. 2	0·0879	25·27	2·989	2·074	0·768	0·915
X. 3	0·0655	26·98	2·527	1·680	0·759	0·847
X. 4	0·0548	29·56	2·392	1·568	0·772	0·824
XXVI. 5	0·0483	31·33	2·387	..	0·874	..
X. 5	0·0331	34·80	1·937	1·126	0·778	0·811
X. 6	0·0134	45·31	1·431	0·609	0·824	0·822
X. 7	0·0096	50·43	1·319	..	0·835	..
X. 8	0·0060	54·16	1·176	..	0·851	..
XX. 3	0·0028	45·38	0·963	..	0·834	..
X. 9	0·0024	54·67	0·954	..	0·823	..
X. 10	0·0006	35·27	0·622	..	0·601	..

this tentatively to the originally acid reaction of the gelatine, and in this he is probably correct, as the acidity is usually due to bisulphites, which are acid to strong bases and basic to strong acids, and of which neutralisation in either sense would probably diminish the original swelling in water. The plates he employed were much thicker (3 to 4 mm. as compared to about 0·25 mm.) than those used in the present research, so that it is doubtful if real equilibrium was reached.

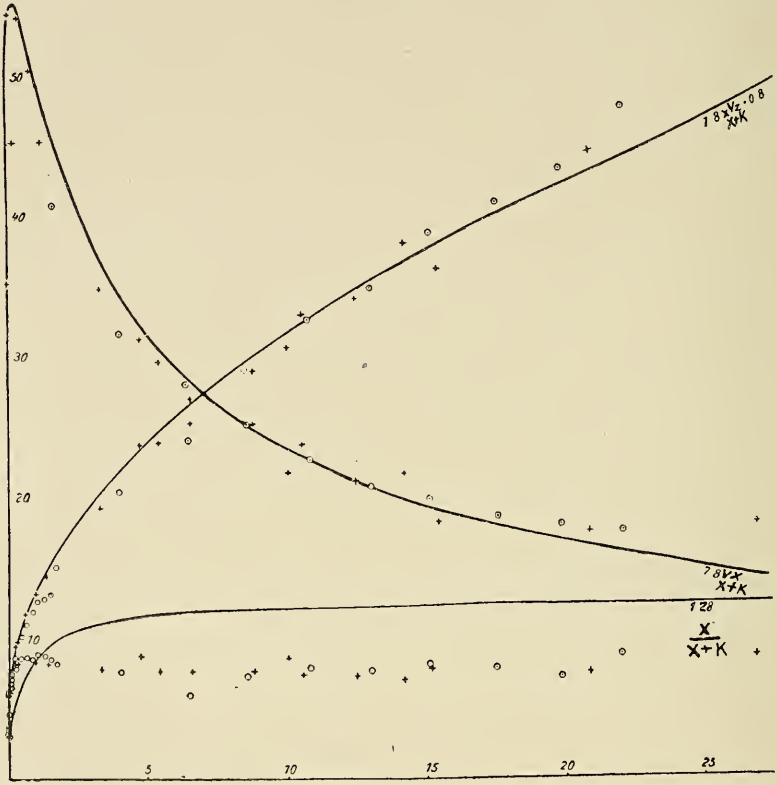

FIG. 123 (Tables III. and IV.).—Abscissæ; mgr.-mols. HCl in 1 grm. solution. Ordinates; + = results from Table III., • = results from Table IV.

Table V. gives the results of a series of experiments intended to test the reversibility of the equilibrium gelatine-acid-water. The gelatine was swollen for forty-eight hours in a solution which, when equilibrium was reached, was of 0·2253 mols. per mil concentration, and then for twenty-four hours in solutions of varied

TABLE IV.—GELATINE AND HYDROCHLORIC ACID

Series No.	Mgr.-mols. HCl in 1 grm. residual solution (Phenolphth.).	Weight of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. HCl absorbed by 1 grm. Dry Gelatine (Phenolphth.)	Mgr.-mols. HCl in 1 grm. solution (Methyl Orange).	Mgr.-mols. HCl absorbed by 1 grm. Dry Gelatine (Methyl Orange).	Mgr.-mols. difference HCl in Gelatine (Phenolphth. and Methyl Orange).	Mgr.-mols. HCl in excess of solution absorbed by Gelatine (Phenolphth.).	Mgr.-mols. HCl in excess of sol. absorbed. Sol. estimated with Methyl Orange.
	a	*b*	*c*	*d*	*e*	*c—e*	*c—ab*	*c—db*
β 1	0·2217	17·63	4·790	0·2193	3·875	0·915	0·876	0·915
2	0·1982	18·12	4·332	0·1964	3·203	1·129	0·734	0·773
3	0·1755	18·74	4·089	0·1733	2·901	1·188	0·793	0·841
4	0·1533	19·92	3·875	0·1516	2·706	1·169	0·817	0·855
5	0·1306	20·74	3·485	0·1286	2·415	1·170	0·770	0·818
6	0·1081	22·75	3·252	0·1066	2·064	1·188	0·788	0·827
7	0·0861	25·13	2·901	0·0841	1·752	1·149	0·733	0·793
8	0·0644	28·23	2·414	0·0625	1·480	0·934	0·593	0·650
9	0·0403	31·65	2·045	0·0386	1·111	0·934	0·763	0·823
10	0·0171	40·81	1·519	0·0154	0·565	0·944	0·821	0·890
α 1	0·0152	30·10	1·315	0·0142	0·610	0·705	0·857	0·888
2	0·0129	32·28	1·298	0·0120	0·498	0·800	0·881	0·890
3	0·0107	37·79	1·268	0·0098	0·520	0·748	0·899	0·903
4	0·0084	38·37	1·196	0·0076	0·409	0·787	0·874	0·904
5	0·0060	36·12	1·096	0·0054	0·352	0·744	0·877	0·901
6	0·0041	37·94	1·016	0·0035	0·352	0·664	0·862	0·883
7	0·0023	33·49	0·860	0·0018	0·194	0·666	0·783	0·793
8	0·0015	31·15	0·751	0·0010	0·000	0·751	0·704	0·720
9	0·0012	26·54	0·685	0·0007	0·000	0·685	0·655	0·668
10	0·0006	18·36	0·467	0·0001	0·000	0·467	0·457	0·466
11	0·0004	9·17	0·304	0·0000	0·000	0·304	0·300	0·304

(lesser) concentration. The latter time does not seem to have been quite sufficient for equilibrium to be again attained, but there is no reason to suppose the absorption as other than completely reversible. The lowness of the "fixed" acid as calculated by deducting the calculated acid of the solution absorbed is somewhat remarkable, and it is unfortunate that in this series no parallel determinations were made with methyl orange. Several possible explanations may be suggested, but it seems best to defer discussion for further experimental investigation. The portions which were only treated for forty-eight hours in one solution are normal in respect of "fixed" acid.

Although no exact quantitative result can be expected from the somewhat crude method of experiment, it is evident that graphic plotting of Tables III. and IV., fig. 123, represents the curves of a regular equilibrium, the figures being fairly consistent for any one series of determinations, and the errors of experiment not greater than may be expected, considering the influence of various undetermined factors, such as the cohesive elasticity of the jelly, and the extremely small forces involved in considerable changes of volume near the swelling maximum. The approximately horizontal course of the "fixed" acid line, after a certain concentration of acid is reached, strongly suggests the idea of a definite though hydrolysing chemical compound, rather than a merely physical one; and the determinations of "fixed" acid by the difference of reaction of phenolphthalein and methyl orange prove a decided change of concentration of the H′ ion at or near that particular point. The occurrence of a very marked maximum of the swelling volume (S) is striking, and this follows naturally from the combination of the two regular curves of total acid per gram of gelatine (a) and of "fixed" acid (f), since by the mode of calculation $S=\frac{a-f}{x}$, x being the concentration of the external solution given in column a.

As regards other acids, only a limited amount of work has been done. With weak acids like acetic and lactic, no definite maximum of swelling has been observed,[1] the absorption of liquid increasing with the concentration till solution of the jelly begins. With formic acid a maximum occurs at a concentration of about 0·07 gram-mols. per liter, but it is less marked, and the rise to it

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[1] It has been since observed by Mr Atkin (*J.S.L.T.C.*, 1920, p. 187) that this occurs with all acids at a P_H of 2·4 of the *external acid* which corresponds very closely with the $P_H=3·0$ of the *gelatin itself* found by Loeb, but this H· concentration was not reached with the very weak acids. (H. R. P.)

Table V.—Gelatine soaked for 48 Hours in HCl of Approx. 0·275 Mgr.-Mols. per Gram, and Nos. 4–16 afterwards for 24 Hours in Weaker Solution

Series No.	Mgr.-mols. HCl in 1 grm. of remaining solution (Phenolphth.).	Weight of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. HCl absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Acid " fixed " by 1 grm. Dry Gelatine.
	a	*b*	*c*	*c*−*ab*=*f*
1	0·2253	20·33	5·411	0·830
2	0·2253	20·14	5·411	0·873
3	0·2253	21·18	5·506	0·734
	Then 24 hours in weaker solutions.			
4	0·2333	22·00	5·683	0·541
5	0·2146	21·61	5·125	0·488
6	0·1950	21·10	4·616	0·502
7	0·1754	22·77	4·567	0·573
8	0·1561	23·44	4·274	0·615
9	0·1383	25·04	4·039	0·576
10	0·1182	24·37	3·531	0·650
11	0·0984	26·89	3·218	0·571
12	0·0807	27·90	2·944	0·692
13	0·0629	28·94	2·465	0·644
14	0·0526	29·33	2·220	0·673
15	0·0476	32·87	2·230	0·667
16	0·0462	31·18	2·083	0·643

is much more gradual than in the case of hydrochloric acid. Owing to the fact that no repression of swelling takes place with the weaker acids, a greater total swelling can be obtained by concentrating the solutions with acetic and probably with lactic acid than with hydrochloric, though it is evidently accompanied with greater solution, and possibly by structural changes of the gelatine.

As regards the fixation of acid, the methyl orange method is inapplicable to any but the strongest acids, but calculating the absorbed solution as of equal strength to the external, figures for the excess-absorption are obtained which for acetic acid of medium concentrations are somewhat lower, and for lactic and formic about the same or slightly higher than those for hydrochloric. At the higher concentrations, the total absorbed acid is so large that experimental error makes the determination of " fixed " acid irregular and unreliable, and from the lowest concentrations the value rises to a fixed average much more gradually than in the case of strong acids.

As regards sulphuric acid, but few determinations have been made, but these show that it produces a maximum swelling effect at a low concentration of which the value has not yet been determined, and the apparently " fixed " acid is also somewhat larger. No experiments have yet been made on the determination of " fixed " acid by methyl orange, but as the change of colour of this indicator is gradual, it is evident that determination by mere titration is somewhat rough, and it is proposed to investigate the subject further by the actual determination of ionisation-constants.

The following tables VI. to IX. give the results of the work which has already been done on acids other than hydrochloric.

Table X. (XXIX. 1–3) gives a few determinations on sheepskin and shows that a maximum exists, the weaker solution swelling more than the stronger ; and the acid " fixed " is very similar in amount to that fixed by gelatine. The skin was unwoolled in the customary way, freed from lime, and dried at 80° C., and soaked in water till soft, before use.

Attention must here be drawn to a research published by Stiasny on the absorption of water and acid by hide-powder and ox-hide [1] by quite different methods to that adopted by the writer. From the data given it would be difficult or impossible to calculate the acid fixed, but the occurrence of a maximum of swelling in the weaker solutions is in both cases very clearly marked. The

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[1] Stiasny, "Ueber negative Adsorption, und die Bestimmung der Schwellwirkung von Säuren auf Hautpulver und Blosse," Gerber, 1909, pp. 183 *et seq.*, and *Collegium*, 1909, pp. 302 *et seq.*

TABLE VI.—GELATINE AND ACETIC ACID

Series No.	Mgr.-mols. of acid in 1 grm. of remaining solution (Phenolphth.).	Weight of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. of acid absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Acid "fixed" by 1 grm. Dry Gelatine.
	a	b	c	$ca-b=f$
XV. 1	0·1050	46·97	5·570	0·638
2	0·0873	44·29	4·520	0·653
3	0·0693	43·90	3·747	0·705
4	0·0513	37·27	2·527	0·615
5	0·0340	32·98	1·679	0·558
6	0·0161	25·36	0·874	0·466
	New Sample of Gelatine,			
A. 1	1·0050	62·97	62·54	−0·74
2	0·5083	57·28	32·05	+2·93
3	0·2062	51·14	11·50	0·95
4	0·1011	44·68	5·127	0·610
5	0·0805	33·89	3·398	0·670
6	0·0512	28·81	2·042	0·395
7	0·0216	20·56	0·917	0·473
8	0·0110	17·35	0·594	0·403

TABLE VII.—GELATINE AND LACTIC ACID

Series No.	Mgr.-mols. of acid in 1 grm. of remaining solution (Phenolphth.).	Weight of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. of acid absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Acid " fixed " by 1 grm. Dry Gelatine.
	a	*b*	*c*	*c*−*ab*=*f*
XVII. 1	0·1047	52·73	6·284	0·764
2	0·0684	48·63	4·124	0·798
3	0·0321	48·19	2·397	0·825
4	0·0048	26·98	0·673	0·543

TABLE VIII.—GELATINE (NEW SAMPLE) AND FORMIC ACID

Series No.	Mgr.-mols. of acid in 1 grm. of remaining solution (Phenolphth.).	Weight of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. of acid absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Acid " fixed " by 1 grm. Dry Gelatine.
	a	*b*	*c*	*c*−*ab*=*f*
B. 1	0·9918	47·90	48·01	0·48
2	0·5196	49·74	26·16	0·31
3	0·1910	53·95	11·33	0·97
4	0·0786	55·92	5·236	0·838
5	0·0511	55·47	3·669	0·834
6	0·0196	47·31	1·640	0·711
7	0·0146	41·40	1·064	0·464

TABLE IX.—GELATINE AND SULPHURIC ACID

Series No.		$\frac{1}{2}$ mgr.-mols. of acid in 1 grm. solution (Phenolphth.).	Weight of solution absorbed by 1 grm. of Dry Gelatine.	$\frac{1}{2}$ mgr.-mols. of acid absorbed by 1 grm. of Dry Gelatine (Phenolphth.).	Acid " fixed " by 1 grm. of Dry Gelatine.
		a	b	c	$c-ab=f$
XVI.	1	0·1055	20·17	3·178	1·050
	2	0·0685	20·85	2·469	1·041
	3	0·0303	25·27	1·855	1·089
	4	0·0024	31·65	0·944	0·868

TABLE X.—SHEEP PELT DRIED AT 80° C. AND HYDROCHLORIC ACID

		Original Solution.					
Series No.		Mgr.-mols. HCl per grm.	Mgr.-mols. NaCl per grm.	Mgr.-mols. HCl in solution.	Weight of solution absorbed by Skin.	Mgr.-mols. HCl absorbed by 1 grm. Skin.	Acid " fixed " by 1 grm. Skin.
				a	b	c	$c-ab=f$
XXIX.	1	0·1466	nil	0·1386	10·38	2·176	0·737
	2	0·0488	nil	0·0466	10·76	1·236	0·735
	3	0·0073	nil	0·0024	19·31	0·467	0·421
XXX.	1	0·1807	3·00	0·1665	5·95	2·389	1·399
	2	0·0907	3·01	0·0798	5·70	1·499	1·044
	3	0·0378	3·02	0	4·71	0·364	0·364
XXXI.	1	0·0692	4·17	0·0580	4·11	1·455	1·217
	2	0·0826	1·66	0·0700	4·27	1·315	1·016
	3	0·0981	0·48	0·0775	3·93	1·227	0·922

results with hide-powder and ox-hide showed considerable divergence, which Stiasny attributes to difference in texture, but which perhaps may have been partly due to the time given having been insufficient to establish complete equilibrium.

One of the most striking effects of the " pickling process " which gave rise to the investigation is the extraordinary dehydration produced by the action of strong solutions of common salt on the acidified skin fibre, and also on the acidified gelatine ; and acidified gelatine is also precipitated by it as a coherent mass from its warm solutions. No such effect is produced by common salt alone on neutral fibre or gelatine, the effect even of saturated solutions being somewhat to increase the swelling—a gelatine absorbing about eight times its weight of water being capable of taking up about eleven of saturated common salt solution, and a larger quantity of one of medium dilution. The results of a series of experiments are given in Table XI. Some other salts, however, and notably ammonium sulphate and some other sulphates, are well known to exercise a powerful dehydrating effect on swollen gelatine or skin, and even to precipitate gelatine from strong warm solutions as a coherent mass. The discussion of these actions of neutral salts must be deferred till the effects of salts in acidified solutions has been more fully considered. It may be pointed out, however, that the effect is most noticeable in the case of sulphates of weak bases, such as ammonium and zinc.

It is unimportant whether the gelatine or skin-fibre is first swollen by acid and then submitted to the action of salt solution, or the proceeding is reversed, since similar effects are produced by the addition of a suitable quantity of acid to the already salted gelatine, and an effective pickling may be produced by adding a calculated quantity of acid to skins placed in a strong brine, although commercially the method is more costly. The quantity of acid which is most effective is larger than that required to produce a maximum swelling, since the presence of salt enables the skin or gelatine to " fix " a larger quantity of acid than it can do in an equally dilute acid solution without salt. In presence of sufficient salt, however, the necessary quantity of acid may be (and commercially usually is) largely exceeded without much interfering with the result, though large excess is undesirable, and in dilute salt solutions diminishes the dehydration. Some instances of the action of acidified salt solutions on skin are given in Table X. (XXX. and XXXI.), and the results of much experimental work on gelatine in presence of hydrochloric acid and salt in different proportions in Tables XII. and XIII.

Comparing the results with those of Tables III. to V. which give the results with hydrochloric acid alone, it will be noted that the total acid absorbed by 1 grm. gelatine is lower, the contraction of volume caused by the salt-expelling acid as well as water ; but, on the other hand, the acid "fixed," as calculated by deducting from the total absorbed acid that contained in a volume of solution equal to that absorbed, is in all cases higher than with hydrochloric acid alone. This does not necessarily

Table XI.—Gelatine and Varying Salt Solution

Series No.	Mgr.-mols. NaCl in solution.	Weight of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. NaCl in swollen jelly of 1 grm. Dry Gelatine.	Salt in excess of that calculated in absorbed solution.
I. 1	3·633	11·90	47·21	3·98
2	3·035	14·72	48·41	3·73
3	2·383	17·08	41·22	0·52
4	1·665	16·42	27·80	0·46
5	0·876	15·11	13·66	0·42
6	0	8·83	0	0

TABLE XII.—GELATINE, HCL AND NACL. ACID APPROXIMATELY CONSTANT, SALT VARIED. THE ORIGINAL ACID WAS IN ALL CASES OF A CONCENTRATION OF 0·0921 MGR.-MOLS. PER GRAM ON THE WATER EMPLOYED, AND THE VARIATIONS ARE CAUSED BY THE ADDITION OF SALT AND THE FIXATION OF ACID BY THE GELATINE DURING THE EXPERIMENT.

Series No.	Mgr.-mols. original HCl per grm. solution.	Mgr.-mols. original NaCl per grm. solution.	Mgr.-mols. HCl in 1 grm. sol. after use (Phenolphth.).	Weight of sol. absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. HCl in jelly of 1 grm. (Dry Gelatine Phenolphth.).	Mgr.-mols. HCl in jelly of 1 grm. Dry Gelatine (Methyl Orange).	Diff. mols. HCl by Methyl Orange and Phenolphth.	Diff. mols. HCl found and calculated from solution absorbed.	Diff. mols. NaCl found and calculated from solution absorbed.
			a	*b*	*c*	*d*	*c*—*d*	*c*—*ab*	*e*
V. 1	0·0694	4·172	0·0628	1·251	1·331	. .	. .	1·252	—0·488
2	0·0723	3·624	0·0677	2·487	1·377	. .	. .	1·209	—0·362
3	0·0757	3·027	0·0696	3·197	1·336	. .	. .	1·114	—0·561
4	0·0790	2·376	0·0758	3·667	1·331	. .	. .	1·053	—0·298
5	0·0829	1·661	0·0793	2·976	1·270	. .	. .	1·034	—1·127
6	0·0871	0·873	0·0834	13·096	1·935	. .	. .	0·926	—1·104
VI. 1	0·0667	4·676	0·0633	1·144	1·313	0·408	0·905	1·241	—1·258
2	0·0694	4·172	0·0631	1·126	1·317	0·750	0·567	1·246	—0·607
3	0·0723	3·624	0·0657	1·275	1·280	0·623	0·657	1·196	—0·325
4	0·0755	3·027	0·0688	1·343	1·249	0·478	0·771	1·157	—0·472
5	0·0790	2·376	0·0741	1·962	1·255	0·710	0·545	1·110	—0·344
6	0·0829	1·661	0·0761	2·816	1·278	0·507	0·771	1·064	—0·670
7	0·0871	0·873	0·0814	10·330	1·831	1·020	0·631	0·990	—0·218
8	0·0894	0·445	0·0853	19·90	2·638	1·640	0·998	0·941	—0·314
9	0·0921	. .	0·0893	31·56	3·525	2·807	0·718	0·707	. .

NOTE.—It would be desirable to repeat the determinations of this table with precautions to ensure that the acid was really constant *after equilibrium was established*. Comparison with Table XIII. shows, however, that the comparatively small variations of acid have in this case but little influence on the results obtained.

TABLE XIII.—GELATINE, HCL AND NACL. ACID VARIED, SALT APPROXIMATELY CONSTANT. THE AMOUNT OF ACID IS DETERMINED AFTER EQUILIBRIUM IS ESTABLISHED, THAT OF SALT IS CALCULATED ON THE ORIGINAL SOLUTION, AS FIXATION IS NEGATIVE AND NEGLIGIBLE AS COMPARED TO THE TOTAL CONCENTRATION.

Series No.		Mgr.-mols. HCl in 1 grm. solution after use (Phenolphthalein).	Wt. of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. HCl in jelly of 1 grm. Dry Gelatine (Phenolphthalein).	Mgr.-mols. HCl in jelly of 1 grm. Dry Gelatine (Methyl Orange).	Diff. mols. acid in jelly by Methyl Orange and Phenolphthalein.	Diff. mols. acid in jelly from that in solution absorbed.	Salt "fixed" by 1 grm. Dry Gelatine.
III.	1	0·0832	1·57	1·239	0·229	1·108	1·108	+0·784
	2	0·0702	1·52	1·228	0·567	0·661	1·121	−0·064
	3	0·0601	1·3	1·257	0·554	0·703	1·175	+0·354
	4	0·0410	1·64	1·199	0·514	0·685	1·132	−0·329
	5	0·0251	2·05	1·138	0·438	0·700	1·087	−0·545
	6	0·0126	2·05	1·102	0·378	0·724	1·076	−0·762
Salt in original solutions 3·02 mols. per gram.								
VII.	1	0·1796	1·54	1·508	0·592	0·916	1·232	−0·912
	2	0·1492	1·58	1·434	0·548	0·886	1·198	−0·853
	3	0·1184	1·52	1·381	0·565	0·816	1·201	−0·885
	4	0·0872	1·60	1·303	0·665	0·638	1·163	−0·620
	5	0·0717	1·58	1·287	0·539	0 748	1·174	−0·495
	6	0·0564	1·58	1·248	0·414	0·861	1·159	−0·731
	7	0·0409	1·50	1·225	0·420	0·805	1·164	−0·690
	8	0·0262	1·50	1·179	0·288	0·891	1·140	−0·629
	9	0·0100	1·57	1·118	0·259	0·839	1·102	..
	10	0·0021	1·62	1·095	0·209	0·886	1·091	−0·735
	11	0·0002	3·16	0·728	..	0·727	0·727	−0·516
	12	..	15·78	0·109 [1]	..	0·109	0·109	+0·180
Salt in original solutions 3·02 mols. per gram.								
VIII.	1	0·1817	13·62	3·495	2·673	0·822	1·020	..
	2	0·1465	12·98	3·028	1·977	1·051	1·127	..
	3	0·1154	12·57	2·553	1·558	0·995	1·102	..
	4	0·0861	11·63	2·088	1·093	0·995	1·087	..
	5	0·0722	10·93	1·842	0·855	0·987	1·052	..
	6	0·0570	11·73	1·698	0·871	0·827	1·029	..
	7	0·0347	11·52	1·426	0·508	0·918	1·026	..
	8	0·0247	10·99	1·295	0·465	0·830	1·024	..
	9	0·0096	10·73	1·142	0·221	0·921	1·039	..
	10	0·0023	9·81	1·010	0·147	0·863	0·987	..
	11	0·0002	10·44	0·684	..	0·684	0·682	..
	12	..	11·90	0·103	..	0·103	0·103	..
Salt in original solutions 0·76 mol. per gram.								

[1] This acidity is original acidity of gelatine, due principally to bisulphites.

imply that the acid actually attracted by the gelatine is greater when salt is present, but that the dissociation or hydrolysation is less, or, on the other hand, that the obviously doubtful assumption that the concentration in acid of the absorbed solution is equal to that of the external is incorrect. If, as is probable, the concentration of the absorbed solution is really less, the apparent "fixed" acid will increase in some inverse ratio to the volume of the solution absorbed.

On the other hand, it must be noticed that the less ionised acid, as determined by its non-effect on the methyl orange, is proportionately, and even actually, less in the salted than in the merely acid solutions. It is, however, by no means probable that methyl orange is wholly insensitive to the acidity of the acid-gelatine, and, unless this is the case, the effect of the latter will be increased by its greater concentration in the contracted jelly, just as methyl orange is reddened by many organic acids in concentrated solution which scarcely affect it when dilute. Any direct action of the acid-gelatine on methyl orange will diminish its apparent "fixed acid" as determined by this means.

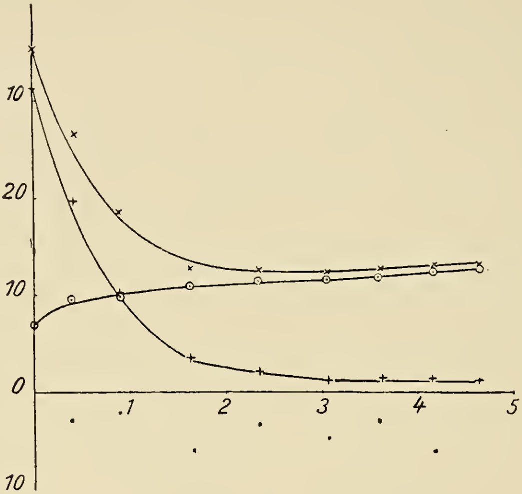

FIG. 124 (Table XII.).—Abscissæ; Mgr.-molecules NaCl in 1 grm. solution. Ordinates; × =Mgr.-mol. HCl in 1 grm. dry gelatine; *o*=concentration of acid fixed by 1 grm. dry gelatine; + =wt. of solution absorbed by 1 grm. dry gelatine; ⊙ =" fixed " salt.

An interesting point in Tables XII. and XIII. is that of the amount of salt "fixed," which in presence of hydrochloric acid appears to be always negative, the few apparent exceptions being obviously due to experimental errors, and accompanied by abnormal figures in one or other of the remaining determinations; while Table XI. shows that in absence of acid, a varying positive amount is "fixed." The quantities were calculated by determining the total chlorine in the treated gelatine with argentic nitrate and potassium chromate, and subtracting from this the hydrochloric acid found acidimetrically, and the total chlorine calculated in the solution absorbed. From the large total amount of chlorides present, and the proportionately large effect of the absorbed solution, great quantitative accuracy cannot be claimed for these figures, but they strongly support the view that the chlorine absorbed as hydrochloric acid by the gelatine exerts a corresponding expulsive effect on the chlorine ions (both acid and salt) contained in the solution. It is noted in connection with the experimental work that in several cases where large quantities of salt were used the sheets of gelatine, instead of appearing homogeneous and transparent, became white and opaque; and this must have been due either to the actual crystallisation of salt in the gelatine, or to the formation of a cellular, or at least heterogeneous structure enclosing solution of a different refractive index to that of the surrounding jelly. It is extremely probable that this circumstance may account for the irregularity of the figures with regard to fixation of salt.

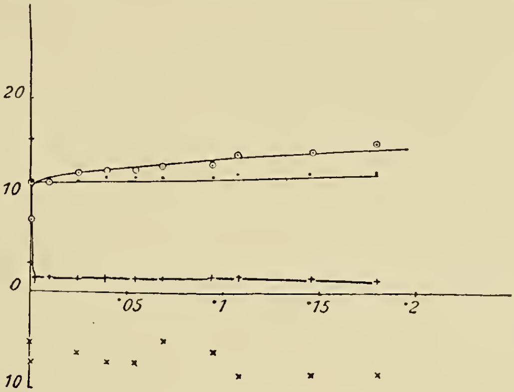

FIG. 125 (Table XIII., series VII.).—Abscissæ; Mgr.-mol. HCl in 1 grm. solution. Ordinates; · = Mgr.-mol. HCl in 1 grm. dry gelatine; + = wt. of solution absorbed by 1 grm. dry gelatine (*b*); ⊙ = "fixed" acid; *x* = "fixed" salt.

From the curves given in fig. 124 it will be seen that the swelling diminishes in a curve of hyperbolic character with increasing concentration of salt, becoming asymptotic to a value apparently somewhat above zero.

Apparently any acid and its corresponding neutral salt will produce a dehydrating effect on swollen gelatine, varying in intensity with the electrolytic dissociation-constant of the acid, and increasing with the concentration of the salt. The effect of sodium sulphate with sulphuric acid appears to be quite as great as that of sodium chloride and hydrochloric acid in equivalent concentrations, while that of the weak acids with their own neutral salts is much less, though distinctly marked when compared to the swelling action of the acids alone, as will be obvious in comparing Tables XV. and XVI. with VI. and VIII. With the weaker acids, the excess of acid absorbed in excess of that due to absorbed solution (" apparent fixed acid ") is much less and very irregular as compared to that observed with the stronger acids ; and this is particularly the case with the feebly ionised acetic acid, of which the ionisation is still further reduced by the presence of its neutral salt.

It is not necessary in order to produce contraction of swelling that the salt employed should have the same anion as the acid, and if the salt is one of a strong acid and in sufficient concentration, good contraction may be obtained even by acidification with very weak acids. Thus effective pickling may be obtained with formic or acetic acid in presence of common salt ; and at the writer's suggestion formic acid has been to some extent used commercially for sheep-skins, as the antiseptic effect is even greater than that of the customary sulphuric acid, while certain injurious effects of the latter on the final manufactured product are avoided. In the ordinary commercial process, as has been stated, sulphuric acid and common salt are employed ; but except for questions of cost, hydrochloric acid and sodium sulphate would be equally effective, as shown in Table XVII. Table XVIII. shows results with acetic acid and common salt. It will be observed that both the dehydration and the acid " fixed " are practically the same with acetic acid as they would have been if hydrochloric acid had been used.

Table XIX. gives a series in which potassium chloride is substituted for sodium chloride with hydrochloric acid. The results are again practically identical with those of sodium chloride.

TABLE XIV.—SULPHURIC ACID AND SODIUM SULPHATE

Series No.	½ mols. H_2SO_4 in residual solution (Phenolphth.).	½ mols. Na_2SO_4 in original solution.	Wt. of solution absorbed by 1 grm. Dry Gelatine.	½ mols. H_2SO_4 in 1 grm. Dry Gelatine after swelling (Phenolphth.).	Excess over acid calculated in absorbed solution.
	a		b	c	$c-ab$
XVIII. 1	0·05342	0·8173	7·072	1·573	1·195
2	0·05446	0·6963	9·840	1·629	1·093
3	0·05668	0·5698	12·75	1·872	1·149
4	0·05773	0·4374	14·42	1·901	1·068
5	0·05883	0·2986	15·44	1·992	1·084
6	0·06053	0·1530	35·18	3·033	0·903

TABLE XV.—GELATINE, FORMIC ACID, AND SODIUM FORMATE. SODIUM FORMATE IN SOLUTION 1·33 MOLS.

Series No.	Mgr.-mols. acid in 1 grm. sol.	Wt. of solution absorbed by 1 grm.	Mols. acid in jelly of 1 grm.	Excess over acid in absorbed sol.
	a	*b*	*c*	*c*—*ab*
D. 1	0·9008	19·45	18·39	0·87
2	0·4955	17·14	9·11	0·62
3	0·2049	15·53	3·79	0·61
4	0·1053	16·04	2·15	0·46
5	0·0824	16·99	1·71	0·31
6	0·0574	15·57	1·23	0·34
7	0·0265	17·07	0·70	0·25
8	0·0172	15·93	0·44	0·17

TABLE XVI.—GELATINE, ACETIC ACID, AND SODIUM ACETATE. SODIUM ACETATE IN SOLUTION 1·33 MOLS.

Series No.	Mgr.-mols. acid in 1 grm. sol.	Wt. of solution absorbed by 1 grm.	Mols. acid in jelly of 1 grm.	Excess over acid in absorbed sol.
	a	b	c	$c-ab$
B. 1	0·9656	20·83	20·64	0·50
2	0·5018	17·64	9·74	0·89
3	0·1991	15·89	3·32	0·16
4	0·1007	14·38	1·56	0·11
5	0·0788	14·20	1·26	0·14
6	0·0526	13·20	0·79	0·10
7	0·0242	12·26	0·39	0·09
8	0·0143	11·05	0·18	0·02

TABLE XVII.—GELATINE, HYDROCHLORIC ACID, AND SODIUM SULPHATE

Series No.		Mgr.-mols. acid per grm. Original solution.	$\frac{1}{2}$ mgr.-mols. Na_2SO_4 per grm. Original solution.	Mgr.-mols. acid in solution after use (Phenolphth.).	Wt. of sol. absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. acid absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Acid "fixed" by 1 grm. Dry Gelatine.
				a	*b*	*c*	*c*−*ab*
XII	1	0·0574	0·8172	0·0560	7·41	1·492	1·067
	2	0·0587	0·6963	0·0524	8·79	1·457	0·941
	3	0·0601	0·5698	0·0533	8·07	1·513	1·028
	4	0·0615	0·4374	0·0558	9·24	1·603	1·035
	5	0·0630	0·2986	0·0555	10·03	1·682	1·050
	6	0·0645	0·1530	0·0565	11·85	1·766	0·937

Original concentration of acid in water only 0·0663 mols.

TABLE XVIII.—GELATINE, ACETIC ACID, AND SALT

Series No.	Mgr.-mols. acid per grm. Original solution.	Mgr.-mols. NaCl per grm. Original solution.	Mgr.-mols. acid in solution after use (Phenolphth.).	Wt. of sol. absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. acid absorbed by 1 grm. Dry Gelatine (Phenolphth.).	Acid "fixed" by 1 grm. Dry Gelatine.
			a	*b*	*c*	$c-ab$
IX. 1	0·0696	4·373	0·0665	1·37	1·166	1·078
2	0·0793	2·371	0·0739	2·65	1·217	1·021
3	0·0874	0·871	0·0839	10·49	1·798	0·918

Original concentration of acid in water only 0·0926 mols.

Table XIX.—Gelatine, Hydrochloric Acid, and Potassium Chloride

Series No.	Mgr.-mols. acid per grm. Original solution.	Mgr.-mols. KCl per grm. Original solution.	Mgr.-mols. acid in solution after use (Phenolphth.).	Wt. of solution absorbed by 1 grm. Dry Gelatine.	Mgr.-mols. acid absorbed by 1 grm. Dry Gelatine.	Acid "fixed" by 1 grm. Dry Gelatine.
			a	b	c	$c-ab$
XIII. 1	0·0551	2·233	0·0524	2·130	1·186	1·069
2	0·0567	1·914	0·0477	2·677	1·207	1·080
3	0·0584	1·576	0·0539	3·732	1·263	1·063
4	0·0601	1·218	0·0555	5·685	1·360	1·044
5	0·0620	0·837	0·0572	11·19	1·664	1·024
6	0·0640	0·432	0·0592	12·26	1·746	1·020

Original concentration of acid in water only 0·0663.

Summary

Gelatine absorbs water with evolution of heat, and is capable of exerting large external pressures in the initial stages, but as the quantity of water becomes greater the avidity of the gelatine becomes less, and there is no further perceptible evolution of heat, while the mechanical force exerted is exceedingly slight, and may be measured in a few dynes per square centimeter. The process is completely reversible, and water may easily be expelled from the fully swollen jelly by mechanical pressure, and completely removed by evaporation *in vacuo*, and to a large extent by dehydrating agents, though as dryness is approached the last portions of water are removed with great difficulty. The swelling does not proceed to infinity in cold water, but reaches a definite maximum, which is an equilibrium between the affinity for water and the elastic cohesive forces of the gelatine, which are influenced not only by its chemical character but by its original volume at setting. In hot water complete solution takes place.

Gelatine is insoluble in, and water-swollen gelatine is impermeable to, strong alcohol, which dehydrates and compresses it. If, however, alcohol is incorporated in the liquid jelly, which is subsequently allowed to set, and immersed in water, the swelling is increased beyond the ordinary maximum.

Gelatine swells in very dilute acids to a much larger extent than in water. In weak acids this swelling increases with the concentration of acid till finally solution takes place, but with strong acids the swelling reaches a maximum at very low dilutions, and subsequently diminishes in a curve of hyperbolic character till the jelly dissolves without further swelling, which limits the possible range of experiment. If, however, a neutral salt of the acid be added, the dehydration may be carried with strong acids to a point at which the gelatine forms a solid and horny mass. With weak acids and their salts the effect is less marked, but quite obvious. If, however, a weak acid is used with large excess of a salt of a strong acid the gelatine behaves as if the strong acid only was present, while gelatine swollen with a strong acid and treated with the salt of a weak one naturally behaves as if the weak acid had been used.

In all cases the acid absorbed by the swelling gelatine is in excess of that due to the absorbed solution, and this excess is in any one series of experiments of an approximately constant amount over a wide range of concentration of the acid or acid and salt solution ; while under no conditions does it pass a maximum of about 1·25 mgr.-mols. of acid per gram of dry gelatine. In the case of strong acids which affect the colour of methyl orange even at very great dilutions, it is shown that a portion of the acid absorbed by gelatine, which varies with the conditions of the experiment but always falls within the limit above stated, has become so considerably less ionised than the free acid that it is incapable of affecting the colour of methyl orange, though it may still be estimated by phenolphthalein.

In the case of common salt it is shown that while in neutral solutions it increases the swelling of gelatine, and an amount is absorbed in excess of that normally contained in the absorbed solution, in presence of even small quantities of hydrochloric acid great dehydration is produced, and the fixation of salt is negative.

Theoretical

As regards the explanation of the foregoing experimental results, anything which can yet be said must, in view of the preliminary character of the investigation and the somewhat rough methods of experiments, be regarded as merely working hypothesis. As a preliminary to this it is necessary to have some definite conception of the actual structure of a gelatine jelly, and the view which is here adopted is that of a network of gelatine molecules cohering to each other, but leaving interstices of molecular dimensions containing water or aqueous solutions, which, being within the range of molecular attractions, are really semi-solid solutions in the gelatine, and have with it a common internal pressure. The gelatine molecule, consisting as it does of a complicated chain of amido-acids, is peculiarly fitted to produce such a structure. The range of molecular attraction does not apparently exceed 10 $\mu\mu$ (millionths of a millimeter), and may be much smaller (*cp.* Freundlich, *Kapillarchemie,* S. 277); but as about 2 per cent. of gelatine is required to form a coherent jelly, there would be in each cubic space of (10 $\mu\mu^3$) a weight of gelatine over thirteen million times the estimated weight of a hydrogen molecule, and therefore ample molecules for a net of molecular dimensions. The facts mentioned as regards the effect of concentration at the moment of setting on the subsequent swelling give considerable support to the idea of a molecular network formed at the time.

This view, though apparently very similar to the currently accepted one of van Bemmelen and Bütschli, is really very different, since these investigators assume a cellular structure of microscopic dimensions, and hence far beyond the range of molecular forces. That such cellular jellies or pseudo-jellies exist and can be produced is undeniable, but in the writer's opinion it is quite unproved that any such structure naturally exists in aqueous gelatine jellies, the microscopic observations all having been made on jellies hardened and shrunk with dehydrating agents, while no structure could be detected in the unhardened jelly, in which its dimensions, if existent, must have been much larger. A dilute gelatine solution which has been sufficiently heated for complete solution shows only stray, and probable accidental, submicrons, and merely a slight Tyndall effect in the ultramicroscope, so that it is probably, for the most part, a true molecular solution in which the gelatine is uniformly distributed throughout the liquid. On cooling no flocculation or visible contraction of the gelatine takes place, but the whole solidifies to a transparent and apparently homogeneous jelly, and it is hard to imagine how, under these conditions, a cellular structure could be formed. In some other cases, as, for instance, in the flocculation of albumin solutions by heat, where the gel is obviously less hydrophile than the sol, the network, even if at first uniform and molecular, necessarily contracts, and a reticular structure must result ; while when a solution separates into two partially immiscible liquids an emulsion will be formed, which may be a pseudo-jelly ; but none of these causes appear to exist with gelatine, and the assumption of a cellular structure does not in any way assist, but considerably complicates the explanation of observed facts.

It is clear that if we accept the conception of a jelly as the solution of a liquid in an elastic solid the whole question of swelling becomes one of osmotic pressures or, perhaps more accurately, one of distribution between two immiscible solvents. In the latter case the common surface takes the place of a semi-permeable membrane, and as the solvents are no longer identical, the partition-constant (*Teilungscoefficient*), and sometimes also a different molecular complexity, have to be considered. There is also an important difference between the two cases which may be overlooked. In ordinary osmosis the molecular attractions of the common solvent merely serve to overcome and balance those of the solute and bring it into a region of equal and common internal pressure, where its kinetic energy can exert itself against a fixed semi-permeable septum, so that in the terms of gas equation V is constant and P varies. In the equilibrium of immiscible solvents, on the other hand, the kinetic energy of the solute is constant, and it is the varying internal attraction of the two solvents for its molecules which determines the partition-constant ; and since the diffusion-surface is freely movable, P is constant and V varies. This latter statement is somewhat modified in the case of jellies by the residual forces of solid cohesion which oppose change of volume. It can be shown, however, that in or near the region of maximum swelling these forces are extremely small. P. von Schroeder [1] showed that a jelly swollen in water lost a large amount of weight and volume (up to 73 per cent.) in an atmosphere of saturated water-vapour, but that this was completely prevented if the jelly were saturated with a N 10^{-5} solution of an alkaline sulphate, and considerably lessened by one of N 10^{-6}. It was subsequently shown by the present writer [2] that the energy involved in removing 1 grm. water against the osmotic pressure of a N 10^{-5} sulphate solution (about 350 ergs) was quite comparable to that done against surface tension in forming the surface of a sphere 1 grm. weight, and that no doubt the shrinkage might be accounted for in that way. It therefore follows that in most cases of considerable swelling the solid cohesion is almost negligible as compared to osmotic forces. On the other hand, in the earlier stages of absorption of water by dry organic colloids, including gelatine, the forces involved are large, as is evidenced by the marked evolution of heat, the contraction of common volume, and the very considerable pressures obtained when the swelling is opposed by mechanical obstacles.

If the swelling of gelatine in pure water be admitted to be osmotic, still more evidently is this the case with regard to the dehydrating action of alcohol on the swollen jelly, since the latter, though freely permeable to water, is practically impermeable to alcohol, and the jelly-mass acts as a simple osmotic cell. The curve of swelling in mixtures of water and alcohol (Table II.) is of a simple type, corresponding closely to a rectangular hyperbola in the middle portion but diverging at both extremes, possibly because of the solid rigidity of the jelly. There is no reason to doubt complete reversibility. Alcohol shows considerable osmotic pressure in an osmometer with gelatine membrane, and it is shown that alcohol incorporated in jelly must produce a cellular structure, in which the jelly acts as a semi-permeable membrane. It is possible that more complete investigation of the dehydrating effects of alcohol on jellies might afford some definite information on their cohesion and osmotic pressures, since the action is purely physical.

The explanation of acid swelling and the peculiar maximum of its curve, and of dehydration of acid gelatine by neutral salts, is much more complex, and involves chemical as well as purely osmotic considerations. In what follows, the most detailed con-

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[1] *Collegium*, 1903, p. 204.

[2] *Brit. Assoc. Rep.*, 1908, p. 216.

sideration will be given to the action of hydrochloric acid and sodium chloride, as these have been most fully investigated, and there is no reason to think that the results differ in principle from those of other acids and their corresponding salts.

Gelatine jelly is known to be very permeable to both acids and salts and to their ions, so that it is not easy to see how either can exert a direct osmotic pressure on the jelly-mass. It has, however, been shown that even very dilute hydrochloric acid is absorbed with some avidity by the jelly, which always contains acid in considerable excess of an equal volume of the surrounding solution with which it is in equilibrium ; and this excess, rising rapidly at first, soon becomes an almost constant quantity (see curve of "fixed acid" in fig. 123), strongly suggesting the idea of a definite though hydrolysing chemical compound of the nature of a salt, in which the amphoteric gelatine acts as base. This idea is further supported by the fact that an approximately corresponding quantity of acid becomes neutral to methyl orange, though it can still be hydrolysed by sufficient excess of water, and estimated by titration with caustic alkali with phenolphthalein as indicator. If such a gelatine chloride exists, it is extremely probable that it will be much less permeable for hydrochloric acid and other chlorides than the neutral gelatine, or, if we regard the jelly as a solution, that the solubility of salts of a common anion in the acid jelly will be much less than in the neutral, while its affinity for water is likely to be greater, owing perhaps to its greater ionisation. The jelly, of course, must be in equilibrium with the surrounding solution in every respect, and firstly in regard to hydrolysis, in which it will obey the ordinary law of mass-action. As regards its volume, the case is quite analogous to that of solutions of an acid and its salt separated by a movable septum permeable to the acid and to water, but not to the salt, which in the present instance is an indiffusible colloid jelly. The two solutions must be in complete equilibrium, and as the salt cannot diffuse, water and acid must pass through the septum till equilibrium is reached. Firstly, then, the common anion must be at equal concentration in both solutions, and because of the salt anions, the free acid must necessarily be less concentrated in the salt solution than in that of the pure acid. Secondly, the anion of the acid in salt solution must be in equilibrium with that of the salt itself, and this can only occur by absorption or expulsion of water or acid till the ionic pressure of the salt is equal to that of the acid contained in its solution. Thus, the necessary data being given, the volume of the salt solution or jelly is definitely fixed, and dependent on the concentration of the acid ions and the ionisation and quantity of the salt. Again, the quantity of unhydrolysed and ionisable salt for a fixed quantity of base depends on the hydrion concentration of the acid and the hydrolysis constant of the salt, and thus different acids with different constants may produce very varied effects of swelling.

One consequence of what has just been said must be remarked. It is evident that the "fixed acid," calculated on the assumption that the absorbed solution is of equal acid concentration to the surrounding acid, does not represent the whole of the unhydrolysed gelatine salt, but is less than it by the amount of acid expelled by the salt from its solution. Whether the whole of this acid is expelled by the ionised salt, or a part also by the un-ionised, which demands water for its solution, is not easy to determine, but probably unimportant for the general theory of the equilibrium.

It is of course impossible to treat the problem at present in any rigid mathematical way while so many of the factors are unknown, and especially that of the cohesive elasticity of the jelly, but it may be interesting to see how far the experimental results agree with theoretical assumptions.

We have assumed that the combination of gelatine with hydrochloric acid is of the nature of a salt of a weak base with a strong acid, of which the hydrolysis, according to Wm. Ostwald, is represented by the equation $\frac{h\mathrm{B}}{b}=\frac{\mathrm{K}_w}{\mathrm{K}_g}=k$, when h is the hydrion concentration, b that of (colloid gelatine) ions, and B of the hydrolysed and unionised base (gelatine). K_w is the dissociation constant of water, K_g that of gelatine as a base. It may be taken without serious error that at the dilutions in question HCl is fully ionised, and that therefore its concentration x in the solution is proportional to h, the concentration of the hydrions. b is the concentration of the kation of the ionised but unhydrolysed salt, and as the quantity of gelatine is constant in the experiment, B is obviously equal to $1-b$. The equation therefore takes the form $\frac{(1-b)x}{b}=k$, and resolving this as regards b, we have $b=\frac{x}{x+k}$ as the measure of the proportion of unhydrolysed salt.[1] The same expression may also be obtained from the ordinary dilution equation $\frac{a^2}{(1-a)v}=k$, which, substituting the hydrolytic for the dissociation constant, also applies to moderate hydrolysis.

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[1] The hydrolysed portion is obviously $\frac{k}{x+k}$.

In this formula a is the hydrolysed portion, which above has been called $1-b$, and $1-a$ is the unhydrolysed salt b, while the concentration of the hydrolysed acid is the same as x, that of the external solution. Substituting these values and resolving as regards b, we again get $b=\frac{x}{x+k}$. It will be observed that v does not appear in this expression, since the concentration is determined by x, and therefore hydrolysis is not affected by the volume of the jelly. The value of b obviously rises rapidly at first and tends to unit value, and the rise is the more rapid and the later part of the curve the more horizontal the smaller the value of k. It must be observed that Ostwald's equation is merely an approximative one, and specially uncertain as complete hydrolysis is approached.

The unit value to which the expression tends is to that of a molecule or equivalent of the salt. In the actual experiments 1 grm. of gelatine was used, and neither its molecular weight nor its valency is known, and it is quite possible that the latter may vary, since as the acid becomes more concentrated it probably attacks additional amino groups.[1] It is impossible to calculate equivalent weights from the direct experiments with hydrochloric acid, since much free acid solution is absorbed in swelling, and it has been shown above that this is not of the same concentration as the external solution. In very dilute external acid the error is not considerable, since the total acid of the solution absorbed is small compared to that fixed by the gelatine, but in this case the hydrolysis is also very large. It has been shown, however, that even with the highest concentrations of acid used the swelling can be reduced to very small proportions by the addition of a sufficient excess of a salt with a common anion (*e.g.* sodium chloride), and as the anion does not increase but depresses the hydrolysis by lessening the ionisation of the salt, we may safely assume that the hydrolysis in this case is almost nil. Under these circumstances we find that the total acid absorbed by 1 grm. of gelatine is about 1·3 mgr.-mols. while that in the absorbed solution does not at most exceed 0·05 mgr.-mols., so that we may roughly assume that under the conditions 1000 mgr. of gelatine

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[1] It may be noted that both Tables III. and IV. show a sudden and rather considerable rise both in the total acid and in the "fixed" acid (as determined by calculation from the volume of the solution absorbed) at the concentration above 0·2 N; and though this may be merely due to experimental error, it is more probable that it is an indication that at about this concentration a further amino-group of the gelatine is attacked, corresponding to its increased solubility in the acid.

combine with 1·28 mgr.-mols. of acid, or, in other words, that the equivalent (though not necessarily the true molecular) weight of the gelatine, considered as monovalent, is about 780. It will therefore be necessary to multiply the values of x by 1·28 to obtain the actual acid combined with the gelatine base.

We may now consider the further question of how the volume of swelling is connected with the absorption of acid. The experimental curve is a very peculiar one with a marked maximum, indicating that at first the swelling increases rapidly with increased concentration, but afterwards diminishes inversely in a slower ratio. According to the theory which has been suggested, the swelling is due to the superior solubility or attraction for water of the ionising gelatine chloride as compared to the non-ionising neutral gelatine, and it should therefore increase directly with the increase of the chloride. On the other hand it is repressed by the anion of the acid solution, which not merely causes the concentration of the jelly with expulsion of water till its total ionic pressure is equal to that of the acid, but also compels the expulsion of free acid from the jelly against the same pressure of x, so that the total anion-pressure of the jelly-mass may remain equal to x. The force required to compress the jelly therefore varies not merely as x but as x^2, and for a given increment of x the swelling should diminish as $\sqrt{x}$. We should expect therefore that swelling would be represented by such an expression as $\beta\frac{x}{x+k}\div\sqrt{x}$, or $\beta\frac{\sqrt{x}}{x+k}$, where x and k have the same values as before, and β is an empirical constant connecting the volume of the jelly with its pressure. Such an expression will obviously give a marked maximum for some small value of x, and by differentiation it is shown that this maximum occurs when $x=k$. We have thus a means of arriving at a value for k, since the experimental maximum is clearly marked at about $x=0{\cdot}005$ N, and the swelling curve on fig. 123 is therefore calculated as $7{\cdot}8\frac{\sqrt{x}}{x+k}$. It is possible that the true value of k is somewhat less than 0·005 N, and that the higher maximum which this would cause is prevented by the cohesion of the jelly; and since the curve rises much more abruptly than it falls, the effect of this rounding off of its summit would be to shift the apparent maximum to a slightly higher concentration; but in any case, if the hypothesis be correct, it cannot be much lower that 0·005, and at least the order of the quantity remains unchanged.

Since $k=\frac{K_w}{K_g}$, and K_w is known, we can calculate an approximate value for K_g, the ionisation constant of neutral gelatine, as $\frac{0{\cdot}6+10^{-14}}{0{\cdot}5+10^{-2}}$, or of the order of 1×10^{-12}. It would be interesting to confirm this by more direct measurement.

Of the direct experimental results, only the value of the total absorbed acid remains to be calculated. This is evidently (from the mode of calculation of the "fixed acid") the sum of the latter and of the volume of absorbed liquid in the jelly multiplied by the concentration of the external solution. As the former approximates closely to 0·8 mols. from the maximum of swelling onwards, and the latter to $x\frac{7{\cdot}8\sqrt{x}}{x+k}$, the curve has been plotted on the sum of these, and sufficiently well expresses the experimental values, but offers no explanation of the amount and constancy of the fixed acid—a question which is discussed in the next paragraph. It is, however, interesting to note that the curve of absorbed acid is also well represented by $y=87\,x^{0{\cdot}41}$, the logarithmic plotting of the smoothed curve being only slightly convex to the origin, and showing that curves quite of the adsorption type may arise as the sum of purely chemical actions.

It has been assumed that the resistance of the jelly to compression by the acid of the outer solution is the product of the direct ionic pressure of the gelatine salt, and of that of the anion of the acid which is expelled along with the water to maintain equilibrium, but which must carry with it its corresponding hydrion. The swelling pressure within the jelly is thus the sum of three partial pressures, of which only one is that of the anion itself, and the acid expelled is therefore only one-third of the total ionised gelatine salt. Since between $x=0{\cdot}5$ and $x=0{\cdot}3$ the quantity of gelatine chloride and its ionisation remain sensibly total and constant, and what change takes place in the one is partially compensated by the corresponding change in the other, the "apparent fixed" and the expelled acid will also remain constant, the one being about 0·8 and the other about 0·4 mols. We have as yet no definite information as to the ionisation of the gelatine salt, the repression of which is no doubt negligible within the limits named, but must become considerable in the presence of much sodium chloride or other salt with a common anion. In this case the acid fixed as un-ionised gelatine salt will increase and that expelled will diminish, so that the curve of fixed acid must more and more closely approach that of the un-ionised gelatine salt, as under these circumstances it is experimentally shown to do.

A point much more difficult of explanation is the almost vertical rise of the fixed acid curve near the origin, and its slight maximum corresponding to that of the swelling curve. It is obvious that the really combined acid cannot exceed that of a correct hydrolysis curve, and no constants or modifications can be adopted for the latter to make its rise more rapid which do not at the same time throw the swelling curve derived from it entirely out of harmony with experiment. It is perhaps a somewhat forced, though not, I think, an altogether improbable, explanation, that the uncombined gelatine at first adsorbs acid without actual combination, and that this adsorption is favoured by the large volume of the jelly at the point of maximum swelling, where the small maximum also occurs on the fixed acid curve. This adsorption would of course tend to increase the apparent fixation of acid and render it more uniform, and would disappear with the disappearance of free base, since it is improbable that the chloride would adsorb hydrochloric acid. Some alternative explanations may be suggested, but it is better to wait the results of further experiment.[1]

It must, I think, be admitted that the complicated system of curves which has been deduced from the theory of actual chemical combination shows an agreement with experimental results which is more than accidental, and which in some sense really represents facts, whether these be strictly chemical or not. It is not to be denied that an equally plausible hypothesis might conceivably be based on physical adsorption, but to be satisfactory it must show a correlation of experimental facts at least as complete as that which has been offered. It is to be admitted that much remains to be done in explaining the still outstanding deviations, in adducing further proof, and in replacing empirical constants by those based on definite knowledge, but the present paper at least provides a working hypothesis. The most marked deviation of fact from theory consists in the more rapid rise of the "fixed acid" to a small maximum above that allowed by the curve of unhydrolysed salt, and disregarding probable imperfections in the dilution equation in such an extreme case, it is suggested that this may be explained by actual adsorption preliminary to chemical combination.

It is obvious that the theory affords a complete qualitative explanation of the dehydrating effect of common salt solutions

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[1] The explanation is completely given by the theory as subsequently developed. See *Trans. Chem. Soc.*, **105**, 1914, p. 325. (H. R. P.)

and other chlorides on gelatine (including skin and connective tissue) swollen with hydrochloric acid, although our knowledge of the laws of concentrated solution is insufficient to enable us to apply the same equations quantitatively. The theory asserts that the falling of the swelling is due to the pressure of the chlorine ions, and it is indifferent whether these are furnished by the acid or some other chloride. That salt not only exerts a compressing pressure on the chloride jelly, but is expelled by the latter from the absorbed solution is proved by the last column in Tables XII. and XIII., in which the fixation of salt is shown to be negative; though in presence of so much salt, the chlorine estimations cannot claim the same degree of accuracy as the acid ones. That salt exercises no compressing but rather a swelling influence on neutral gelatines is shown by Table XI., in which also the salt absorption is positive. The effect of salt in raising the apparent acid "fixed" is also easy of explanation, since the presence of the chlorine ion limits hydrolysis by repressing ionisation and increasing un-ionised chloride, and prevents expulsion of acid from the absorbed solution by being itself expelled in its place. A question arises, however, as to whether the compression of the jelly under these circumstances should be treated merely as a case of ionic equilibrium, or not rather as a "salting out," in which the avidity for water of the different constituents is more important than their ionic pressure, and in which the un-ionised as well as the ionised sodium chloride plays its part. Throughout, it has been assumed in the equations that the whole of the gelatine chloride, and not merely its ionised or un-ionised part, is effective in the swelling; but obviously, if the ionisation is comparable to that of most salts, it must practically total up to concentrations such as were used in the acid experiments.

It remains, however, to be considered whether the theory developed from the study of hydrochloric acid is one of general applicability to all acid swelling of gelatine or gelatinous tissues, or whether it is merely an exceptional case confined perhaps to a few of the stronger acids, since sulphuric acid and sulphates show completely parallel effects (see Table IX.).

It has been often stated that since a swelling effect was common to all acids of sufficient hydrion concentration, the hydrion must be regarded as the active swelling agent; but this in the light of the present theory must be regarded as only indirectly the case, since the hydrion concentration is the measure of the avidity, and hence of the salt-forming avidity of the acid; and it is quite possible that, as in the case of ammonium salts and many other organic bases, not only the anion but the hydrion enters into the salt. In all cases the anion is the compressing and dehydrating agent; and in the absence of a neutral salt, a maximum with subsequent contraction is produced by the acid itself. This is, however, only obvious in the case of the stronger acids, since the weak acid, although it may produce a gelatine salt, is so little ionised that its anion cannot reach a sufficient concentration to overcome the pressure of the more ionised gelatine salt. Thus, while sulphuric acid produces a marked maximum, that of formic acid, though still obvious, is much less distinct, and with acetic and lactic acids none is observable, and the swelling continues to increase with concentration, becoming in the end greater than that produced by the stronger acids, and going on without a break to the final solution of the gelatine. In these cases the apparent "fixed acid" is somewhat variable, sometimes higher and sometimes lower than that of strong acids according to whether the ionic concentration is sufficient to prevent hydrolysis or to attack additional amino groups.

It may be objected that sodium or potassium chlorides will produce vigorous dehydration not only with hydrochloric acid, but with any other acid of sufficient hydrion concentration to produce swelling; but a little reflection makes it obvious that any such combination simply leads to a quadruple equilibrium in which each acid is balanced against its own neutral salt. Thus in the case of acetic acid and sodium chloride we have gel-ions, acet-ions, and an enormous excess of sodium and chlorine ions, and if we imagine combination, we must by the law of mass-action have much gelatine chloride balanced against sodium chloride and little gelatine acetate against sodium acetate. Hence the rule, since the salt is always largely in excess, that with the salt of a strong acid the dehydrating effect is the same whether the acidification has been by a weak or a strong acid, and *vice versa*. Acetic or formic acid will produce as effective a pickling with common salt as sulphuric or hydrochloric acid.

As regards other acids and their salts it has been shown that in all cases depression of swelling is caused by a sufficient addition of the neutral salt, but this is most marked with the salts of the stronger acids, possibly because with weak acids the ionisation of the salt added is insufficient to repress that of the gelatine compound itself.

I do not propose in this paper to discuss the complicated effect of the action of salts on the swelling of neutral gelatine which has been specially investigated by Pauli, Hofmeister, von

Schroeder and others,[1] but it may be suggested that it is quite conceivable that in many cases a portion of the salt undergoes dissociation or hydrolysis, and that both acid and base combine with the gelatine, and that the compound so formed swells or is compressed by the remaining salt solution according to its concentration. Paessler [2] has shown that sodium acid sulphate is dissociated by hide-substance, only the neutral salt remaining in solution, and it is clearly proved in the case of chromic, ferric, and aluminic salts that a similar action takes place in which both acid and base (or a basic salt) are absorbed. This absorption of base may occur either by combination with opened-up COOH groups, or as complex salts such as are often formed by ammonia with other bases; and some of these may form complex ions which are unrepressed by those of the simple salt in solution.

The subject of alkaline swelling is also left untouched, but it is clear from some preliminary experiments that in certain respects it differs radically from acid swelling. For instance, swelling by sodium hydrate is not at all repressed by sodium chloride [3] but is so by higher concentrations of the hydrate, showing that in this case hydroxyl ions and not the kation Na are the swelling and repressing agents. It is hoped to pursue the question of alkaline swelling.

It is obvious that the facts discussed in the paper have an important bearing on many physiological questions, and in this connection a crude attempt made in the early stages of the inquiry to imitate muscular contraction may be worthy of mention. A slender spiral platinum electrode was embedded in a cylinder of jelly which was immersed in a salt solution containing a second electrode. When the gelatine electrode was the anode of a sufficient current to electrolyse the salt the jelly contracted admirably, but its relaxation by a reverse current was somewhat unsatisfactory owing to the evolution of hydrogen, which broke up the gelatine. No doubt with a suitable depolariser better results might be attained, and it is quite possible that the condensation of the anion by a mere surface potential difference might be sufficient to produce the effect.

Pauli [4] has recently published a paper on albumen in which he

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[1] Pauli (Paseheles), *Pflug. Arch.*, 1898, **71**, 336 u. 339. Pauli u. Rona, *Beitr. z. Chem. Physiol. u. Pathol.*, 1902, **2**, 25–26. Hofmeister, *Arch. für experim. Pathol. u. Pharmacol.*, 1888, **24**, 424. Von Schroeder, *Collegium*, 1902, p. 306.

[2] *Wissenschaftliche Beilage des Ledermarkt*, 1901, ii. 106.

[3] This has been shown by later work to be not strictly true, though the repression is very much less than in the acid equilibrium. (H. R. P.)

[4] *Zeitschrift für Chem. u. Ind. der Kolloide*, 1910, S. 241.

supports very similar views to those just expressed, though laying more weight on the hydration of the colloid ion than has been done in the present work. In particular he strongly advocates the molecular as opposed to the cellular or network structure claimed by Bütschli. He also mentions the fact that acid jellies cannot be dehydrated by pure alcohol, which has been confirmed in the present investigation, though it has also been found that with acidified alcohol considerable contraction takes place.

PART II.—THE ACID-GELATINE EQUILIBRIUM [1]

By H. R. Procter and J. A. Wilson

In an earlier paper by one of us (*Transactions*, 1914, **105**, 313, *Journal of the American Leather Chemists' Association*, 1914, pp. 207–25) it was shown that gelatine forms hydrolysable salts with acids, that swelling is due to the ionisation of these and the osmotic pressure so produced, and that an equilibrium results, in which the concentrations of anion, hydrion, and ionised gelatine salt can all be expressed as functions of the concentration of acid in the external solution, within the limits of experimental error. In this earlier paper the concentration of the ionised gelatine chloride in the equilibrium gelatine-hydrochloric acid was shown to be approximately $Clg = \sqrt{0{\cdot}02x + 0{\cdot}0002}$, where Clg was the chlorine ionised from the gelatine salt, and x the concentration, in terms of normality, of the external hydrochloric acid. (Through an error Clg was given as $\sqrt{2x + 0{\cdot}02}$, but all actual calculations were made from the above formula.) It was also assumed that the numerical values in the expression were constants, as those adopted sufficiently closely represented the experimental results then quoted, but closer theoretical investigation has shown that this is not strictly the case, but that both Clg and x are functions of a quantity e, which is the difference in osmotic pressure between two phases of which the ionic products are equal, but in one of which the factors are unequal, and that it is this difference which causes the swelling of the jelly.

In the paper cited, the hydrochloric acid and gelatine salt were, for the sake of simplicity, supposed to be wholly ionised, and as the ionisation in both cases is very high and the solutions were dilute, such an assumption was quite justifiable as regards experimental results. In the closer theoretical examination which we now propose, however, we must define the concentrations as

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[1] *Transactions of the Chemical Society*, 1916, pp. 307 ff.

referring only to the actual ions; and we shall again first consider the comparatively simple case of hydrochloric acid and gelatine, where the ionisation is in reality almost complete.

The following system of notation will be employed :—

At equilibrium :

In the external solution :

$x=[H^+]=[Cl']$.

In the jelly phase :

$y=[H^+]$.

z=concentration of gelatine ions.

$y+z=[Cl']$.

a=concentration of non-ionised gelatine chloride.

g=sum of concentrations of gelatine, gelatine chloride, and gelatine ions.

e=excess of concentration of diffusible ions of the jelly over that of the external solution.

V=volume of the jelly in c.c.

All concentrations are expressed in gram-equivalents per liter. In all experiments 1 grm. of dry gelatine was immersed in 100 c.c. of the acid solution and allowed to remain for forty-eight hours to reach equilibrium, the temperature being about 20° in each case. The concentration of acid in the external solution was determined by titration, and that in the jelly by titrating the solution expelled from the jelly by the addition of salt, and with these, knowing the initial concentration of the acid and the percentage of ionisation of acid in the external solution, the actual ionic concentrations can be calculated.

In a two-phased equilibrium, such as the present, two different equations must be fulfilled. It is necessary that the products of hydrion and chloridion should be equal in the two phases, that is

$$x^2=y(y+z) \quad . \quad . \quad . \quad . \quad (1)$$

This is not only proved by the thermo-dynamical equation of Donnan, quoted in the earlier paper (*loc. cit.*), but also follows from the ordinary laws of ionisation, since the non-ionised portion of hydrochloric acid which, although small, must exist, takes no direct part in the equilibrium, and must be equal in both phases since the jelly is permeable to it, and

$$x^2=[H_1^+]\times[Cl'_1]=K[HCl]=[H_2^+]\times[Cl'_2]=y(y+z).$$

It was, however, previously pointed out that the equations

$$\begin{cases} x^2=y(y+z) \\ 2x=2y+z \end{cases}$$

cannot simultaneously be fulfilled, since in the jelly $[H^+]$ and $[Cl']$ are necessarily unequal, the chlorion being greater than the hydrion by the amount z, and the sum of the sides of an unequal rectangle in necessarily greater than that of the sides of a square of equal area (see fig. 126). In other words, $2y+z$ is greater than $2x$ by an amount we shall call e, and the corrected equation becomes

$$2x+e=2y+z \quad . \quad . \quad . \quad . \quad (2)$$

The concentration of diffusible ions of the jelly is therefore greater by e than that of the outer solution. It is obvious, since water and hydrogen chloride can pass freely into the jelly, that there must be some force equal to and opposing the osmotic pressure produced by this excess e of concentration at equilibrium, for otherwise the jelly would tend to swell to infinity.

Before attempting to speculate about the nature of this opposing force, we must consider its mathematical relations to the other concentrations of the equilibrium as defined by equations (1) and (2). The general theory of the equilibrium as developed in earlier papers (this book, p. 117, and *J.A.L.C.A.*, 1914, pp. 207-25) is that when gelatine is placed in dilute acid it absorbs it freely and forms a hydrolysing salt, the proportion of which to the whole gelatine base present is determined by the hydrolysis equation. The gelatine salt, like other salts, is highly ionised into the anion and a colloid kation, which either from polymerisation or other causes peculiar to the colloid state cannot diffuse and exerts no measurable osmotic pressure, whilst its anion is retained in the jelly by the electro-chemical attraction of the colloid ion, but exerts osmotic pressure which, on the one hand, causes the mass to swell with absorption of the external solution, and, on the other, expels a portion of the acid, both anion and hydrion, from this solution absorbed, the result in equilibrium being that the jelly is poorer in hydrion and more concentrated in anion than the external acid solution, the difference of concentration between anion and hydrion in the jelly being, of course, equal to the ionised anion of the gelatine salt, and electrically balanced by the positive gelatine ions; whilst the hydrion concentration in the jelly is less concentrated than that of the outer solution by the amount of acid expelled, which may be called v (the isotonic volume of hydrion or chlorion expelled at a concentration of x); v bears the simple relation to y that $y+v=x$, and the concentration of ionised gelatine chloride, $z=2v+e$.

By solving simultaneously equations (1) and (2) the following interesting relations are derived :—

$$x=y+\sqrt{ey}=\sqrt{y^2+yz}=\frac{z^2-e^2}{4e}$$

$$y=\frac{-z+\sqrt{z^2+4x^2}}{2}=\frac{2x+e-\sqrt{4ex+e^2}}{2}=\frac{(z-e)^2}{4e}$$

$$z=\frac{x^2-y^2}{y}=\sqrt{4ex+e^2}=e+2\sqrt{ey}$$

$$e=\frac{(x-y)^2}{y}=z+2y-2\sqrt{y^2+yz}=-2x+\sqrt{4x^2+z^2}.$$

These relations can be represented graphically for any value of x, as is shown in fig. 126.

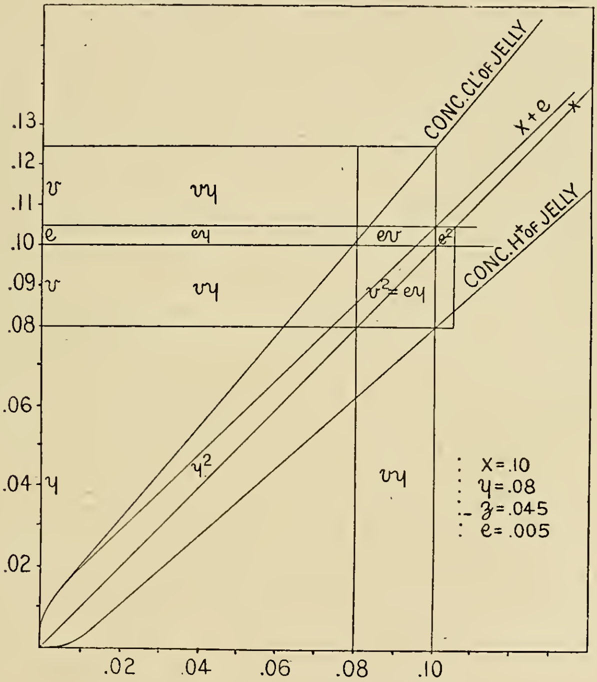

FIG. 126.—Curves of Concentration.

Any one variable can be derived in terms of any other two, but in no case, from only the two equations given, can an equation be derived containing only two variables. As was pointed out previously, however, z was found from experiment to be equal approximately to $\sqrt{0{\cdot}02x+0{\cdot}0002}$, which bears a resemblance to one of the derived equations, namely, $z=\sqrt{4ex+e^2}$. Putting $e=0{\cdot}005$ we get $z=\sqrt{0{\cdot}02x+0{\cdot}000025}$, which is strikingly like the one obtained empirically, but gives low values for concentrations less than $x=0{\cdot}03$. Theoretical considerations rendered it improbable that e, considered in the general way in which we have done, could be a real constant, but it is difficult to obtain a smooth experimental curve from the formula $e=\frac{(b-y)^2}{y}$, because small errors in y correspond with large errors in e, and it is not possible to determine y in the most dilute solutions with very great accuracy by volumetric methods.

It occurred to us, however, that if we could incorporate the volume of the jelly, which can be determined with great accuracy, into an equation containing only two other variables, it would at once be possible to calculate any variable from V and x only. It was found that the theory could be summed up in the form of such an equation, which could readily be subjected to the rigid test of experiment. The notation used is that mentioned earlier in this paper. The degree of ionisation of any given electrolyte, MN, is often expressed by the formula $[\mathrm{M}^+]\times[\mathrm{N}']=K[\mathrm{MN}]$, where K may be nearly constant, as in the case of acetic acid, or a variable, as in the case of highly ionisable electrolytes. In the following, gelatine chloride is considered to be ionised into gelatine ion and chloridion, and the gelatine ion to be ionised still further into gelatine molecule and hydrion. A similar case would be the ionisation of ammonium chloride into ammonium, and chlorion and the further ionisation of the ammonion into ammonia and hydrion. We may therefore write :

(*a*) $$[\text{gelatine ion}]\times[\mathrm{Cl}']=K[\text{gelatine chloride}]$$
$$\text{or } z(y+z)=Ka.$$

(*b*) $$[\text{gelatine molecule}]\times[\mathrm{H}^+]=K'[\text{gelatine ion}]$$
$$\text{or } y(g-a-z)=K'z.$$

By solving (*a*) and (*b*) simultaneously to remove the term in a :

(*c*) $$Kgy=y^2z+Kyz+yz^2+KK'z.$$

Taking Procter's figure of 839 for the molecular weight of a unit of gelatine, 1 grm. of gelatine represents 0·00119 gram-equivalent. Therefore at any volume :

(*d*) $$g=\frac{1{\cdot}19}{V}.$$

Substituting (*d*) in (*c*) and simplifying :

(*e*) $$V=\frac{1{\cdot}19\,Ky}{z(y^2+Ky+yz+KK')}.$$

Or in terms of x and y:

$$(f) \qquad V=\frac{1\cdot19\,Ky^2}{(x^2-y^2)\,(x^2+Ky+KK')}.$$

The value for K' has been considered to be so small that neglecting it should produce no appreciable errors in concentrations greater than $x=0\cdot005$, so that for these more concentrated solutions the equation reduced to:

$$(g) \qquad V=\frac{1\cdot19\,Ky^2}{(x^2-y^2)\,(x^2+Ky)}.$$

Now K has been assumed, with good reason, to be nearly equal to the ionisation-constant of hydrochloric acid for corresponding concentrations. It will be noted from the above equation that small errors in the value of K will produce negligible errors in the calculations so long as the value of Ky is considerably greater than that of x^2, and such a condition does obtain in these more concentrated solutions so long as K is the ionisation-constant of a strong electrolyte. For the present set of calculations, then, it will be permissible to take K as the ionisation-constant of hydrochloric acid, which is known approximately for any given concentration. Moreover, since it has been shown that, in these more concentrated solutions, almost all the gelatine has been converted into the monochloride, we are justified in taking K as the ionisation-constant of hydrochloric acid at concentration g, where g is simply $\frac{1\cdot19}{V}$. Now, from experimental values for V and x it is possible to calculate values for y, which should not differ from the value obtained from experiment by more than would be attributed to experimental error. The results are given in Table I.

The agreement between experimental and calculated values bears out the theory remarkably well, the differences being not greater than was to be expected, considering the difficulties in titrating small quantities of solutions containing traces of organic matter. We feel that values for e calculated from V and x by this formula will be approximately correct. Of course it is evident that in the very dilute solutions K' ceases to be a negligible quantity. Preliminary experiments with the hydrogen electrode show that K' is of the order of $0\cdot00015$, which fully justifies our assumptions in neglecting it for the higher concentrations.

In figs. 127 and 128 curves are given for the various variables as functions of x. The values of V, x, and y were obtained directly from experiment, whilst those of z and e were calculated by

TABLE I.

Determined as noted above.[1]	By Experiment.			Calculated.
K	V	x	y	y
0·95	16·9	0·262	0·228	0·237
0·94	17·5	0·220	0·186	0·195
0·88	20·2	0·174	0·145	0·152
0·85	21·6	0·153	0·123	0·132
0·85	21·6	0·130	0·105	0·108
0·83	22·4	0·108	0·080	0·087
0·80	24·1	0·087	0·066	0·068
0·75	25·9	0·064	0·049	0·047
0·65	34·3	0·0386	0·028	0·026
0·56	45·6	0·0165	0·0084	0·0084
0·55	49·4	0·0118	0·0057	0·0050
0·50	56·4	0·0071	0·0020	0·0022

means of the above formula. It will be noted by reference to figs. 127 and 128 that e apparently varies directly as the volume. Such a relation, if it could be proved, would simplify all other relations to the extent that any variable could be expressed, with suitable constants, in terms of any other one, and the theory, as such, might well be said to be complete.

It was conceived that by means of the hydrogen electrode we could determine all the variables in a special experiment in which the volume was kept more nearly constant. One grm. of gelatine was dissolved in such a quantity of water that at 33° the volume was 21 c.c. This high temperature was used because it is necessary to make hydrion determinations in the melted jelly. The method of using the hydrogen electrode was similar to that used and described by Sörensen. Acid was added at intervals and the hydrion concentration determined. From the figures obtained it was found possible to calculate all the variables desired. Knowing the quantity of acid added, it was possible to calculate, from the hydrion concentration found, the amount which had combined with the gelatine, and consequently the total concentration of gelatine chloride, giving values for y and $a+z$. Whilst actually there is no external solution, there is a theoretical one, since the products of hydrion and chloridion must be equal in both phases; that is, the product $y(y+z)$ of the jelly is equal to the x^2 of the theoretical external solution.

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[1] These calculations are based on the figures of Bray and Hunt (*Journ. Amer. Chem. Soc.*, 1911, 33, 781) and those of Noyes and Falk (*ibid.*, 34, 454).

If, as before, we regard the gelatine chloride as ionised to about the same extent as hydrochloric acid, we can take K as the ionisation-constant of hydrochloric acid at a concentration of

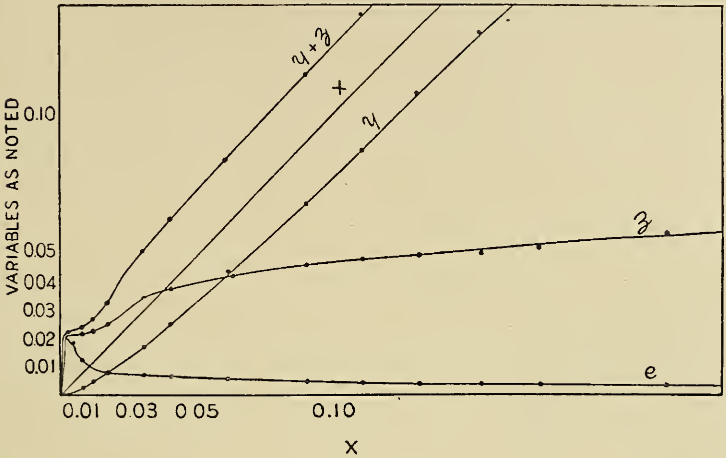

FIG. 127.

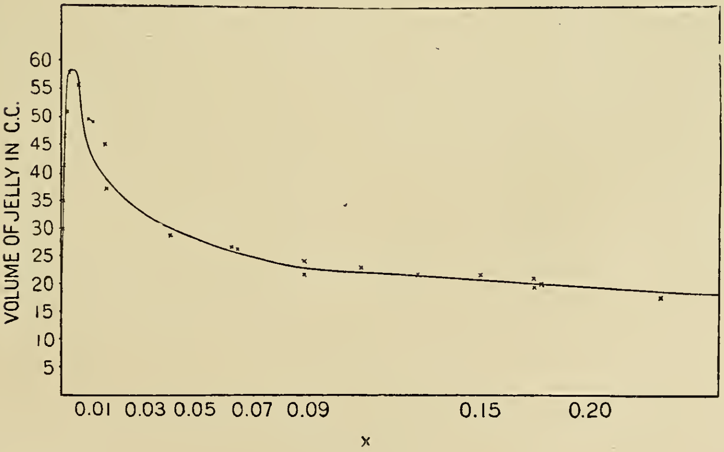

FIG. 128.

$a+z$, which is known. From the equation $z(y+z)=Ka$ it follows that

$$z=\frac{-(K+y)+\sqrt{(K+y)^2+4K(a+z)}}{2}$$

in which all terms on the right-hand side are known, and consequently z can be calculated. From y and z, also, all other variables can be calculated by formulæ presented earlier in this paper. The results obtained in this way are given in Table II, and are shown graphically in fig. 129.

The curve of special interest is that of the variable e, which is seen to increase to a maximum at a very low concentration and then to fall in a manner similar to that of the volume curve (fig. 128). Since e represents the measure of an outward pressure, we have, when the jelly is free to swell, an application of a special case of Hooke's Law, *ut tensio sic vis*, where stress $= e \times$ strain; and since e is a uniform pressure, it follows that it will produce an increase in the size of the jelly, but not in its shape, and that the increase in volume will be directly proportional to the pull. If we take the volume of 1 grm. of dry gelatine as 0·7 c.c., then, so long as the elastic limit is not exceeded, $e = k(V - 0{\cdot}7)$, where the value of the constant is determined by the bulk modulus of the gelatine or particular protein under consideration. The relation is therefore dependent on the temperature, and that this is an appreciable factor is shown by the rough experiments tabulated on the following page.

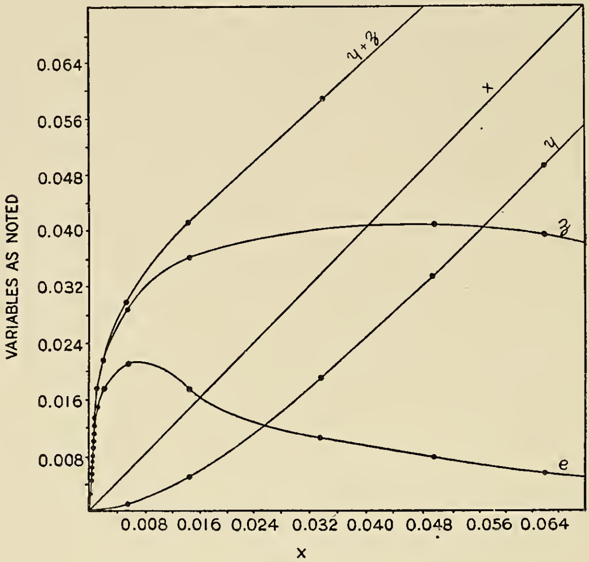

FIG. 129.

It is probable that the effect produced by this limited rise of temperature is not due to material changes in ionisation or chemical activity, but almost solely to the diminution of the solid

Initial concentration of Acid.	Volume of Jelly.		
	7°	15°	33°
0·200	11·3	17·6	..
0·100	13·0	19·8	..
0·050	14·6	23·2	33·0 [1]
0·025	18·5	27·3	..
0·010	22·2	34·3	..

cohesion of the jelly. Many reasons convince us that the cohesive forces of the jelly opposing e are still maintained beyond the melting point.

It is evident that the volume of the jelly, at a constant temperature, is dependent for its value on the value of e, and the only remaining question is why the value of e should follow a curve of the particular type that it does. As was noted earlier in this paper, the following equation results from a simultaneous solution of the thermo-dynamic and osmotic equations given :

$$e = -2x + \sqrt{4x^2 + z^2}.$$

As the concentration of acid is increased from zero to some small, but finite, value, z must necessarily increase at a very much greater rate than x. This is shown very markedly in the most dilute solutions, where almost all the acid added combines with the gelatine ; but z has a limiting value, which is determined by the total concentration of gelatine with which we started. Now z must either approach this limiting value or diminish, which it would do if the ionisation of the gelatine chloride were sufficiently repressed. In either case

$$\underset{x=\infty}{\text{limit}} \sqrt{4x^2+z^2} = \sqrt{4x^2} = 2x$$

from which it follows that :

$$\underset{x=\infty}{\text{limit}} e = -2x + 2x = 0.$$

It is clear from this that, as x increases from zero, e must increase to a maximum and then decrease, approaching zero asymptotically, regardless of whether or not the ionisation of the gelatine salt is appreciably repressed. In fig. 129 it will be seen that e begins to decrease at a considerable rate while z is still increasing slightly, which would be expected. It should be noted that the

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[1] The value for the volume of 33°, a temperature well above the melting point of the jelly, is approximate only, and was obtained by gradually raising the temperature of the swollen jelly and its equilibrium acid, when the jelly, from its gravity and viscosity, does not mix with the supernatant liquid.

TABLE II.

c.c. $N/_2$–HCl added.	Volume produced. V	Concentration of acid produced.	Concentration hydrion found. y	Concentration of acid found.	Concentration of acid combined. $a+z$	z	x	e	$y+z$
0·0	21·0	..	0·000003	..	..	..	..	..	..
0·1	21·1	0·002381	0·000006	0·000006	0·002375	0·002351	0·000119	0·002128	0·002357
0·2	21·2	0·004762	0·000011	0·000011	0·004751	0·004614	0·000226	0·004202	0·004625
0·3	21·3	0·007143	0·000016	0·000016	0·007127	0·006965	0·000334	0·006320	0·006981
0·4	21·4	0·009345	0·000030	0·000030	0·009315	0·009064	0·000522	0·008069	0·009094
0·5	21·5	0·011628	0·000046	0·000046	0·011582	0·011229	0·000718	0·009817	0·011275
0·6	21·6	0·013888	0·000048	0·000048	0·013840	0·013390	0·000803	0·011875	0·013438
0·8	21·8	0·018348	0·000117	0·000117	0·018231	0·017665	0·001442	0·015005	0·017782
1·0	22·0	0·022727	0·000246	0·000247	0·022480	0·021555	0·00232	0·01741	0·021801
1·4	22·4	0·031250	0·00100	0·00101	0·03024	0·02881	0·00559	0·02107	0·02981
2·0	23·0	0·043478	0·00501	0·00511	0·03837	0·03621	0·01437	0·01748	0·04122
3·0	24·0	0·062500	0·0193	0·0201	0·0424	0·03928	0·0336	0·01059	0·0586
4·0	25·0	0·080000	0·0335	0·0350	0·0450	0·04098	0·0500	0·00813	0·0745
5·0	26·0	0·096154	0·0492	0·0521	0·0440	0·03935	0·0660	0·00573	0·0886

apparent decrease in z in the most concentrated solution, given in Table II., is due chiefly to the increased volume.

An interesting point is raised here regarding the action of salt in repressing the swelling of jelly swollen with acid. Whilst the salt undoubtedly represses the ionisation of the gelatine chloride to some extent, it would scarcely be sufficient to account for the fact that salt reduces the volume of jelly almost to that of dry gelatine. The chief action is probably that the addition of salt corresponds with an increase in the value of x, and that this increase in x must, according to the equation just discussed, produce a decrease in the value of e, with a corresponding diminution of the volume of the jelly.

Summary

When gelatine is immersed in a dilute solution of an acid combination takes place between the gelatine molecules and the hydrogen ions, resulting in the formation of a highly ionisable salt of gelatine, the anion of which in tending to diffuse exerts on the jelly mass an outward pull, which, being uniform in all directions, produces, according to Hooke's Law, an increase in the volume of the jelly proportional to the magnitude of the pull. In the case of gelatine immersed in a very dilute solution of a highly ionisable acid (say, 1 grm. of gelatine in 100 c.c. of N/1000 hydrochloric acid) almost all the acid combines with the gelatine, and we have the simplest type of equilibrium, where, practically, $x=0$, $y=0$, $y+z=z=e$, and the concentration of the anion of the jelly is the measure of the outward pull and consequently of the increase in volume. In more concentrated acid solution (say, 1 grm. of gelatine in 100 c.c. of N/10 hydrochloric acid) only a part of the acid combines with the jelly, and we have $y+z>z>e$, but here it is neither the total concentration of anion of the jelly nor that of the ionised gelatine salt which is the measure of the force producing swelling, but it is the excess of concentration of diffusible ions of the jelly over that of the external solution. This quantity e is a direct measure of the swelling so long as the swelling does not exceed the elastic limit, and offers a complete explanation of the peculiar swelling curve obtained by immersing gelatine in increasing concentrations of hydrochloric acid (see fig. 128). In the most dilute solutions e will increase almost directly with the increasing initial concentration of acid, but will approach a maximum as the formation of the gelatine monochloride nears completion, and must then decrease as x becomes larger, according to the equation

$e = -2x + \sqrt{4x^2 + z^2}$, where z has a limiting maximum value. The repression of swelling by the addition of salt is caused by the apparent increase in the value of x produced, which results in a diminution of the value of e and consequently in a repression of the swelling, this action being assisted to some extent by the repression of the ionisation of the gelatine salt.

In the case of weak acids, like acetic, a greater total concentration of the acid is required to produce nearly complete combination of the gelatine with the acid, because the degree of combination is determined by the value of y, which, even in the more concentrated solutions, will be small because of the repression of the ionisation of the acid by the highly ionisable gelatine salt. For this reason the swelling of gelatine in acetic acid increases with increasing total concentration of acid, and is not repressed by the addition of an excess ; in fact, the swelling continues up to a strength of acid of N/1, beyond which solution of the gelatine takes place. The somewhat stronger formic acid actually shows slight repression, whilst very weak acids, such as boric, as would be expected, produce little, if any, swelling.

In pure water, combination must take place, although probably only to a very slight extent, between the gelatine molecules and the hydrion of the slightly dissociated water, leaving in the jelly a corresponding excess of hydroxyl ions which tend to diffuse outward, causing the jelly to swell. The presence of sulphites in the gelatine and carbonic acid in the water tend, of course, to produce a greater swelling than the minimum, which would result from pure gelatine and water, difficult, if possible, to obtain.

Some work has been done on the equilibrium of gelatine and alkalies, but solution of the gelatine took place at so low a concentration of the alkali (at about $x = 0{\cdot}04$ for sodium hydroxide at 20°) that the work could not be carried out to the extent desired. Work on hide has shown that the swelling is repressed either by the addition of excess of alkali or by the addition of ammonium chloride. In the former case the swelling is repressed by the increase in the value of x, according to the law derived for acids ; in the latter case by bringing the solution back almost to a condition of neutrality, the gelatine compound being again decomposed. It is probable that the laws governing alkaline swelling are the same as those governing acid swelling.

It will be seen that the laws discussed are quite general, and that for any particular sample of gelatine at constant temperature any variable can be expressed as a direct function of x, and that for all acids the value of K' will be the same, whilst the value of K is merely dependent on the degree of ionisation of the gelatine salt formed. With suitable values for K, K', and k, the laws are probably applicable to any protein and any acid or alkali.

If, as the authors believe, the foregoing theory is not merely applicable to gelatine, but, with appropriate constants to the colloidal swelling of all proteins, it is obviously of far-reaching importance, not merely to the special technology in which it originated, but to many physiological and medical problems. It is only necessary to allude to the work of Loeb on the fertilisation of the *Echinus* egg by saline solutions, of Fischer on œdema, and of Pauli and others who attribute muscular energy to colloidal swelling and contraction produced by the alternate action of sarcolactic acid and the saline constituents of the blood ; whilst many of the problems of plant growth and of the semi-permeability of vegetable membranes are probably due to analogous causes ; and the laws which regulate the swelling of carbohydrate jellies, such as agar-agar, starch, and cellulose itself, demand a similar investigation.

APPENDIX C

COAL-TAR DYESTUFFS SUITABLE FOR DYEING AND STAINING VEGETABLE AND CHROME TANNED LEATHER

By Mr M. C. Lamb, F.C.S., Director of the Light Leather Department, Leathersellers' Company's Technical College, Tower Bridge Road, London, S.E.1

Abbreviations of the names of dye manufacturers :—

A. Alliance Colour and Chemical Co., Radnor Street Works Stretford, Manchester.
B. British Dyestuffs Corporation, Blackley, Manchester.
C. The Clayton Aniline Co., Ltd., and The Society of Chemical Industry in Basle, Clayton, Manchester.
Ca. John Campbell & Co., 75 Hudson Street, New York, U.S.A.
Co. The Colne Vale Dye and Chemical Co., Ltd., Milnsbridge, Huddersfield.
D. E. I. du Pont de Nemeurs & Company Inc., Wilmington, Delaware, U.S.A.
G. J. R. Geigy S.A., Basle, Switzerland.
H. L. B. Holliday & Co., Ltd., Huddersfield.
L. London Dye Manufacturing Co., Ltd., City Mills, High Street, Stratford, London, E.
S. J. B. & W. R. Sharp, Ltd., Lumb Works, Edenfield, Lancs.
Sa. Sandoz Chemical Works, Basle, Switzerland.
Y. Yorkshire Dyeware and Chemical Co., Ltd., Kirkstall Road, Leeds.

DYEING

Single Acid Colours suitable for Dyeing Vegetable-tanned Leathers

Browns

Acid Brown 79186 (B).
,, ,, 79487 (B).
,, ,, B. (C).

Manilla Brown (B).
Nut Brown D. (B).
,, ,, Y. (B).

Browns—(continued)

Acid Brown G. (C).
,, ,, L. 348 (C).
,, ,, 1580 (C).
,, ,, RN. (G).
,, ,, L. 600 (S).
Leather Brown G. (A).
,, ,, SX. (A).
Leather Tan Brown (A).
Orion Brown G. (S).
Resorcine Brown A. Conc. (B).
Resorcine Brown (C).
,, ,, G. (G).
,, ,, A. (B).
,, ,, (H).
Tan Brown RR. (B).
Light Tan (L).
Dark Tan (L).

Yellows

Acid Yellow 79210 (B).
Airedale Yellow (Y).
Azo Yellow I. (C).
,, ,, (Ca).
Azoflavine C. (C).
,, 7032 (C).
Citronine Y. Conc. (B).
,, R. ,, (B).
,, OOO. (C).
Fast Leather Yellow C. (C).
,, ,, 4G. (C).
,, ,, R. (C).
Kiton Yellow R. (C).
,, ,, S. (C).
,, ,, SR. (C).
,, ,, G. (C).
,, ,, 2G. (C).
Leather Yellow SX. (A).
Metanil Yellow S. (Ca).
Naphthol Yellow S. (C).
,, ,, S. (Ca).
Tartrazine (C).
,, (Ca).
,, S. (H).
,, Pure (H).
,, N. (H).
,, (H).
Tartraphenine (Sa).
Quinoline Yellow (C).
Kiton Fast Yellow G. (C).
,, ,, 2G. (C).
,, ,, 3G. (C).
,, ,, R. (C).

Oranges

Aceko Orange II. (Ca).
Acid Orange G. (B).
Crocein Orange SX. (A).
Kiton Fast Orange G. (C).
,, ,, 2R. (C).
Orange II. (H).
,, II. (B).
Orange II. (C).
,, II. (Sa).
,, II. (A).
,, II. (S).
,, MNO. (C).
,, R. (C).

Scarlets

Aceko Scarlet R. (Ca).
,, ,, 2R. (Ca).
,, ,, 3R. (Ca).
Leather Scarlet (A).
Ponceau R. (H).
,, 2R. Conc. (H).

Scarlets—(continued)

Aceko Scarlet 4R. (Ca).
,, ,, 2G. (Ca).
Coomassie Milling Scarlet G. (B).
Coomassie Scarlet 9012K. (B).
Croceine Scarlet 9187K. (B).
,, ,, (Ca).
Ponceau 4R. (H).
Ponceau SS. (L).
Scarlet R. (B).
,, 2R. (B).
,, 3R. (B).
,, 50 (B).
,, 2R. (S).
Milling Scarlet 5B. (B).

Reds

Aceko Fast Red (Ca).
Acid Milling Red G. Conc. (G).
Acid Milling Red R. Conc. (G).
Acid Magenta NS. (Co).
Acid Red 903 (S).
Acid Rhodamine R. (C).
,, ,, 2R. (C).
,, ,, 3R (C).
Brilliant Sulphon Red B. (Sa).
Cardinal Red J. (B).
,, ,, 3B. (B).
Claret Red (Ca).
Fast Leather Red PSNR. (C).
,, ,, C. (C).
,, Red A. (A).
,, ,, A. Ex. (A).
,, ,, S. Ex. (A).
,, ,, A. Ex. (S).
,, ,, EAS. (B).
Kiton Red S. (C).
,, ,, G. (C).
,, ,, 6B. (C).
Roccelline (C).
,, (Ca).
Toney Red B.D. (B).

Bordeaux

Azo Rubine (Sa).
,, ,, (Ca).
Benzyl Bordeaux B. (C).
Bordeaux B. (A).
Brilliant Bordeaux B. (H).
Carmoisine (Ca).
Carmoisine Conc. (Sa).
Erio Fast Fuchsine BL. Conc. (G).
Helianthine G. (G).
Jasmine (G).
Pure Bordeaux B. (B).

Blues

Aceko Blue CY. (Ca).
Benzyl Blue S. (C).
,, ,, B. (C).
Fast Acid Blue RH. (B).
Fast Leather Blue L. (C).
,, ,, AI. (C).
,, ,, ARI. (C).
Induline (C).
Kiton Fast Blue V. (C).
Leather Blue RR. (A).
,, ,, SX. (A).
,, ,, BB. (A).
Marine Blue (H).
Orion Blue (S).
Soluble Blue NS. (Co).
,, ,, A. (A).

Blues—(continued)

Induline BL. (Co).
,, Crystals L. 332 (S).
,, A. (B).
,, 2B. (B).
,, 5B (B).
Soluble Blue (Ca).
,, ,, 3M. (B).
Solid Blue B. (G).
Xylene Blue VS. (Sa).

Greens

Acid Green B. Ex. (C).
,, ,, G. Ex. (C).
Alizarine Cyanine Green F. Powder (B).
Azo Dark Green A. (G).
Benzyl Green B. (C).
Direct Green L. 854 (S).
Erioglaucine A. (G).
,, Ex. (G).
Erio Green B. (G).
Kiton Fast Green V. (C).
Leather Green SX. (A).
Lissamine Green B. (B).
Naphthol Green (Ca).
,, ,, 9211K. (B).
New Fast Acid Green (Ca).
Wool Green S. (Sa).
,, ,, S. (C).

Violets

Aceko Violet 4B. (Ca).
,, ,, 10B. (Ca).
Acid Violet 6B. (G).
,, ,, 4BNS. (Sa).
,, ,, 3BN. (C).
,, ,, 4BN. (C).
,, ,, 6BN. (C).
,, ,, 7B. (C).
Benzyl Violet 5R. (C).
,, ,, 4B. (C).
,, ,, 5BN. (C).
Benzyl Violet 6B. (C).
,, ,, 10B. (C).
Coomassie Violet R. (B).
Direct Violet L. 723 (S).
Fast Leather Violet 4R. (C).
Fast Sulphon Violet 5BS. (Sa).
Kiton Fast Violet 10B. (C).
Leather Violet (L).
Victoria Violet (C).

Blue-Blacks and Blacks

Acid Black 4BNN. (C).
,, ,, HA. (C).
,, ,, PR. (C).
,, ,, PB. (C).
,, ,, (Ca).
Coomassie Black DW. (B).
Fast Sulphon Black F. (Sa).
Naphthalene Black 12B. (B).
,, ,, B. (B).
,, ,, BD. (B).
Naphthol Blue Black (C).
,, ,, B. Conc. (G).
Naphthol Black ESN. (S).
Nigrosine G. Crystals (B).
,, B. Conc. (S).
,, ES. Crystals (S).
,, Crystals W. (Co).
,, S. (A).
,, B. (A).
,, A. (C).
,, B. (C).
,, K. (C).
,, S. 1471 (C).

Single Basic Dyes suitable for Dyeing Vegetable-tanned Leathers

Browns

Basic Brown BXN. (D).
,, ,, GX. (D).
,, ,, 1557 (C).
Bismarck Brown R. 100s. (B).
,, ,, G. (C).
,, ,, R. (C).
,, ,, M. (C).
,, ,, 8634 (S).
,, ,, (A).
,, ,, R. Conc. (H).
,, ,, R. (H).
,, ,, G. (H).
,, ,, R. Conc. (Co).
,, ,, Y. (Ca).
,, ,, R. (Ca).
Brown A.T. (G).
Canelle 1352 (C,
Canelle 3373 (C).
,, 5733 (C).
,, 8337 (C).
,, 63N. (C).
,, OF. (C).
,, ES. (C).
Chocolate Brown 3936 (C).
,, ,, MNB. 86 (C).
Havanna 352 (C).
Leather Brown A. (C).
,, ,, G. (C).
,, ,, 135 (C).
,, ,, 3378 (C).
,, ,, 4183 (C).
,, ,, 8669 (C).
Vesuvine GS. (Sa).

Yellows

Acridine Yellow R. (H).
,, ,, 2R. (H).
Auromine O. (Sa).
,, O. (H).
,, O. Conc. (H).
,, II. (H).
, O. (B).
,, II. (C).
,, O. (C).
,, OO. pure (C).
,, O. (G).
,, O. (D).
,, Conc. (D).
,, (Ca).
Brilliant Phosphine G. (C).
Brilliant Phosphine 2G. (C).
,, ,, 5G. (C).
,, ,, R. (C).
Patent Phosphine G. (C).
,, ,, 2G. (C).
,, ,, M. (C).
,, ,, R. (C).
,, ,, GGMK.(C.)
Saba Phosphine G. (Sa).
,, ,, 2G. (Sa).
Sella Flavine G. (G).
,, ,, R. (G).
Sella Brilliant Yellow P. Conc. (G).
Tannoflavine T. (Sa).

Oranges

Acridine Orange L. (B).
Chrysoidine YRP. (B).
,, GS. (Sa).
,, R. (G).
,, R. (A).
Chrysoidine R. (D).
,, 1606 (S).
,, G. (D).
,, (Ca).
Pure Chrysoidine YD. (Co).

Reds

Magenta 87952 (B).
,, (C).
Russian Red B. (C).
,, ,, G. (C).
Rhodamine B. (C).
,, G. (C).
,, 6G. (C).
,, B. (D).
Rhodamine B. Ex. (D).
Safranine GOOO. (C).
,, MN. (C).
,, BS. (H).
,, RFF. (H).
,, Y. (Ca).
Tannin Pink C. (B).

Blues

Basic Marine Blue (Ca).
Bengal Blue R. (G).
Fast Blue 3R. (Sa).
Methylene Blue 2B. (B).
,, ,, ZF. (B).
,, ,, BBH. (H).
,, ,, BB. Ex. (H).
,, ,, R. Ex. (H).
,, ,, 2B. (Sa).
,, ,, D. (G).
Methylene Blue XD. (D).
,, ,, B. (D).
,, ,, 1565 (S).
,, ,, (Ca).
Turquoise Blue G. (B).
Victoria Blue BX. (D).
,, ,, Conc. (D).
,, ,, B. Base (D).
,, ,, B. (Ca).

Greens

Basic Green B. Conc. (H).
,, ,, G. Conc. (H).
Fast Green O. (C).
,, ,, YYO. (C).
Malachite Green Crystals A. (B).
Malachite Green Crystals (Ca).
Methylene Green B. (H).
Methylene Green G. (H).
,, ,, P. (C).
,, ,, G. Ex. (Sa).
,, ,, (G).
Victoria Green Small Crystals (D).
Victoria Green B. Powder (D).

Violets

Crystal Violet Powder (D).
,, ,, Base (D).
Methyl Violet NE. (D).
,, ,, 6B. (Ca).
,, ,, 2B. (Ca).
,, ,, 4B. (Ca).
,, ,, (A).
,, ,, 2B. Conc. (S).
,, ,, BE. (G).
Methyl Violet 6B. Conc. (H).
,, ,, 2B. Conc. (H).
,, ,, 2B. (B).
,, ,, 10LB. (B).
Violet RN. (C).
,, R. (C).
,, 3R. (C).
,, B. (C).
,, 5BO. (C).

Blacks.

French Black 67445 (H).
Jute Black G. Conc. (H).
Leather Black A. (Sa).
,, ,, CII. (C).

Leather Black SM. (C).
,, ,, CBD. (C).
Nigeria Black BX. (D).
,, ,, GX. (D).

STAINING

Single Acid Colours suitable for Staining Vegetable-tanned Leathers

Browns

Acid Brown 79186 (B).
,, ,, B. (C).
,, ,, G. (C).
,, ,, L. 348 (C).
,, ,, 1580 (C).
,, ,, RN. (C).
,, ,, L. 600 (S).
Leather Brown G. (A).
,, ,, SX. (A).

Leather Tan Brown (A).
Orion Brown G. (S).
Resorcine Brown A. Conc. (B).
Resorcine Brown (C).
,, ,, G. (G).
Tan Brown RR. (B).
Light Tan (L).
Dark Tan (L).

Yellows

Acid Yellow 79210 (B).
Airedale Yellow (Y).
Azo Yellow I. (C).
,, ,, (Ca).
Azoflavine C. (C).
,, 7032 (C).

Citronine OOO. (C).
Leather Yellow SX. (A).
Metanil Yellow S. (Ca).
Naphthol Yellow S. (C).
,, ,, S. (Ca).
Tartraphenine (Sa).

Oranges

Aceko Orange II. (Ca).
Acid Orange G. (B).
Crocein Orange SX. (A).
Orange II. (H).
,, II. (C).

Orange II. (A).
,, II. (Sa).
,, II. (S).
,, MNO. (C).
,, R. (C).

Scarlets

Aceko Scarlet R. (Ca).
,, ,, 2R. (Ca).
,, ,, 3R. (Ca).
,, ,, 4R. (Ca).
,, ,, 2G. (Ca).

Coomassie Scarlet 9012K. (B).
Leather Scarlet (A).
Scarlet 50 (B).
,, 2R. (S).
Croceine Scarlet (Ca).

Reds

Aceko Fast Red (Ca).
Acid Milling Red G. Conc. (G).
Acid Milling Red R. Conc. (G).
Acid Magenta NS. (Co).
Acid Red 903 (S).
Brilliant Sulphon Red B. (Sa).
Cardinal Red 3B. (B).
Claret Red (Ca).
Fast Leather Red PSNR. (C).
,, ,, C. (C).
,, Red A. (A).
,, ,, A. Ex. (A).
,, ,, S. Ex. (A).
,, ,, A. Ex. (S).
,, ,, EAS. (B).
Roccelline (C).
,, (Ca).

Bordeaux

Azo Rubine (Sa).
,, ,, (Ca).
Benzyl Bordeaux B. (C).
Bordeaux B. (A).
Brilliant Bordeaux B. (H).
Carmoisine (Ca).
Carmoisine Conc. (Sa).
Erio Fast Fuchsine BL. Conc. (G).
Helianthine G. (G).
Jasmine (G).
Pure Bordeaux B. (B).

Blues

Aceko Blue CY. (Ca).
Benzyl Blue B. (C).
,, ,, S. (C).
Disulphine Blue 87724 (B).
Fast Leather Blue L. (C).
,, ,, AI. (C).
,, ,, ARI. (C).
Induline (C).
,, BL. (Co).
,, Crystals L. 332 (S).
,, A. (B).
Induline 5B. (B).
Leather Blue RR. (A).
,, ,, SX. (A).
,, ,, BB. (A).
Marine Blue (H).
Orion Blue (S).
Soluble Blue 3B. (B).
,, ,, NS. (Co).
,, ,, A. (A).
,, ,, (Ca).
Solid Blue M. (G).

Greens

Acid Green B. Ex. (C).
,, ,, G. Ex. (C).
,, ,, (B).
Azo Dark Green A. (G).
Benzyl Green B. (C).
Direct Green L. 854 (S).
Erioglaucine A. (G).
,, Ex. (G).
Erio Green B. (G).
Leather Green SX. (A).
Lissamine Green B. (B).
Naphthol Green (Ca).
,, ,, 9211K. (B).
New Fast Acid Green (Ca).
Wool Green S. (Sa).
,, ,, S. (C).

Violets

Aceko Violet 4B. (Ca).
,, ,, 10B. (Ca).
Acid Violet 6B. (G).
,, ,, 4BNS. (Sa).
,, ,, 3BN. (C).
,, ,, 4BN. (C).
,, ,, 6BN. (C).
,, ,, 7B. (C).
Benzyl Violet 5R. (C).
,, ,, 4B. (C).
Benzyl Violet 5BN. (C).
,, ,, 6B. (C).
,, ,, 10B. (C).
Coomassie Violet R. (B).
Direct Violet L. 723 (S).
Fast Leather Violet 4R. (C).
Fast Sulphon Violet 5BS. (Sa).
Leather Violet (L).
Victoria Violet (C).

Blue-Blacks and Blacks

Acid Black 4BNN. (C).
,, ,, HA. (C).
,, ,, PR. (C).
,, ,, PB. (C).
,, ,, (Ca).
Fast Sulphon Black F. (Sa).
Naphthalene Black 12B. (B).
,, ,, B. (B).
,, ,, BD. (B).
Naphthol Blue Black (C).
Naphthol Blue Black B. Conc. (G).
Naphthol Black ESN. (S).
Nigrosine G. Crystals (B).
,, B. Conc. (S).
,, ES. Crystals.
,, Crystals W. (Co).
,, S. (A).
,, B. (A).
,, A. (C).
,, B. (C).
,, K. (C).
,, S. 1471 (C).
,, SS. (B).

Single Basic Dyes suitable for Staining Vegetable-tanned Leathers

Browns

Basic Brown BXN. (D).
,, ,, GX. (D).
,, ,, 1557 (C).
Bismarck Brown R. 100s. (B).
,, ,, G. (C).
,, ,, R. (C).
,, ,, M. (C).
,, ,, 8634 (S).
,, ,, (A).
,, ,, R. Conc. (H).
,, ,, R. (H).
,, ,, G. (H).
,, ,, R. Conc. (Co).
Canelle 3373 (C).
,, 5733 (C).
,, 8337 (C).
,, 63N. (C).
,, OF. (C).
,, ES. (C).
Chocolate Brown 3936 (C).
,, ,, MNB.86(C).
Havanna 351 (C).
Leather Brown A. (C).
,, ,, G. (C).
,, ,, 135 (C).
,, ,, 3378 (C).

Browns—(continued)

Bismarck Brown Y. (Ca).
,, ,, R. (Ca).
Brown A. T. (G).
Canelle 1352 (C).
Leather Brown 4183 (C).
,, ,, 8669 (C).
Vesuvine GS. (Sa).

Yellows

Acridine Yellow R. (H).
,, ,, 2R. (H).
Auromine O. (Sa).
,, O. (H).
,, O. Conc. (H).
,, II. (H).
,, O. (B).
,, II. (C).
,, O. (C).
,, OO. pure (C).
,, O. (G).
,, O. (D).
,, Conc. (D).
,, (Ca).
Brilliant Phosphine G. (C).
Brilliant Phosphine 2G. (C).
,, ,, 5G. (C).
,, ,, R. (C).
Patent Phosphine G (C)
,, ,, 2G. (C).
,, ,, M. (C).
,, ,, R. (C).
,, ,, GGMK. (C).
Saba Phosphine G. (Sa).
,, ,, 2G. (Sa).
Sella Flavine G. (G).
,, ,, R. (G).
,, Brilliant Yellow P. Conc. (G).
Tannoflavine T. (Sa).

Oranges

Acridine Orange L. (B).
Chrysoidine YRP. (B).
,, GS. (Sa).
,, R. (G).
,, R. (A).
Chrysoidine R. (D).
,, 1606 (S).
,, G. (D).
,, (Ca).
Pure Chrysoidine YD. (Co).

Reds

Magenta 87952 (B).
,, (C).
Russian Red B. (C).
,, ,, G. (C).
Rhodamine B. (C).
,, G. (C).
,, 6G. (C).
,, B. (D).
Rhodamine B. Ex. (D).
Safranine GOOO. (C).
,, MN. (C).
,, BS. (H).
,, RFF. (H).
,, Y. (Ca).
Tannin Pink C. (B).

Blues

Basic Marine Blue (Ca).
Basic Blue (C).
Bengal Blue R. (G).
Methylene Blue XD. (D).
,, ,, B. (D).

Blues—(continued)

Fast Blue 3R. (Sa).
Methylene Blue 2B. (B).
,, ,, ZF. (B).
,, ,, BBH. (H).
,, ,, BB. Ex. (H).
,, ,, R. Ex. (H).
,, ,, 2B. (Sa).
,, ,, D. (G).
Methylene Blue 1565 (S).
,, ,, (Ca).
,, ,, G. (C).
Turquoise Blue G. (B).
Victoria Blue BX. (D).
,, ,, Conc. (D).
,, ,, B. Base (D).
,, ,, B. (Ca).

Greens

Basic Green B. Conc. (H).
,, ,, G. Conc. (H).
Fast Green O. (C).
,, ,, YYO. (C).
Malachite Green Crystals A. (B).
Malachite Green Crystals (Ca).
Methylene Green B. (H).
Methylene Green G. (H).
,, ,, P. (C).
,, ,, G. Ex. (Sa).
,, ,, (G).
Victoria Green Small Crystals (D).
Victoria Green B. Powder (D).

Violets

Crystals Violet Powder (D).
,, ,, Base (D).
Methyl Violet NE. (D).
,, ,, 6B. (Ca).
,, ,, 2B. (Ca).
,, ,, 4B. (Ca).
,, ,, (A).
,, ,, 2B. Conc. (S).
,, ,, BE. (G).
Methyl Violet 6B. Conc. (H).
,, ,, 2B. Conc. (H).
,, ,, 2B. (B).
,, ,, 10LB. (B).
Violet RN. (C).
,, R. (C).
,, 3R. (C).
,, B. (C).
,, 5BO. (C).

Blacks

French Black 67445 (B).
Jute Black G. Conc. (H).
Leather Black A. (Sa).
,, ,, CII. (C).
,, ,, 1722 (C).
Leather Black SM. (C).
,, ,, CBD. (C).
Nigeria Black BX. (D).
,, ,, GX. (D).

Acid Mixtures suitable for Dyeing and Staining *Browns* upon Vegetable-tanned Leathers

Resorcine Brown A. Conc. (B).
Acid Yellow 79210 (B).
Naphthol Green 9211K. (B).
Dark Tan (L).
Azoflavine C. (C).
Acid Green G. Ex. (C).

Acid Mixtures suitable for Dyeing and Staining *Browns* upon Vegetable-tanned Leathers—*continued*

Manilla Brown (B).
Citronine R. Conc. (B).
Wool Green S. (Sa).

Resorcine Brown G. (G).
Leather Yellow SX. (A).
Erioglaucine A. (G).

Orange II. (H).
Tartrazine (H).
Kiton Fast Green V. (C).

Basic Mixtures suitable for Dyeing and Staining *Browns* upon Vegetable-tanned Leathers

Bismarck Brown 8634 (S).
Chrysoidine 1606 (S).
Fast Blue 3R. (Sa).

Bismarck Brown G. (C).
Canelle 1352 (C).
Fast Green O. (C).

Bismarck Brown R. (B).
Auromine O. (B).
Malachite Green Crystals A. (B).

Vesuvine GS. (Sa).
Auromine O. (Sa).
Fast Blue 3R. (Sa).

Chrysoidine R. (G).
Auromine O. (G).
Bengal Blue R. (G).

Bismarck Brown 8634 (S).
Chrysoidine 1606 (S).
Direct Green L. 854 (S).

Bismarck Brown R. Conc. (Co).
Pure Chrysoidine YD. (Co).
Malachite Green Crystals A. (B).

Chrome Leather

The following dyestuffs are suitable for dyeing chrome leather. The leather, after tanning, is washed, neutralised with borax, sodium bicarbonate, or washing soda, re-washed, and then mordanted by drumming or paddling in a tannin solution.

The following are recommended proportions for various shades of colour :—

Dark brown shades, 3 per cent. gambier, 1 per cent. fustic extract.
Medium brown shades, 2 per cent. gambier, 2 per cent. fustic extract.
Light brown shades, 2 per cent. gambier, 3 per cent. fustic extract.

The leather is dyed immediately after mordanting ; the fat-liquoring operation is best done after the dyeing has been completed.

Dyes suitable for dyeing Chrome-tanned Leathers

Acid Colours, dyed in a weak sulphuric or formic acid solution

Browns

Acid Brown RN. (G).
,, ,, 79186 (B).
,, ,, 79487 (B).
,, ,, B. (C).
,, ,, G. (C).
,, ,, L. 348 (C).
,, ,, 1580 (C).
Manilla Brown (B).
Nut Brown D. (B).
,, ,, Y. (B).
Resorcine Brown N. (G).
,, ,, A. Conc. (B).
Resorcine Brown (C).
,, ,, G. (G).
,, ,, A. (B).

Yellows

Acid Yellow 79210 (B).
Acid Orange G. (B).
Airedale Yellow (Y).
Azoflavine C. (C).
Azoflavine 7032 (C).
Leather Yellow SX. (A).
Tartrazine (C).
,, S. (H).

Reds and Maroons

Benzyl Bordeaux B. (C).
Cardinal Red J. (B).
,, ,, 3B. (B).
Fast Leather Red C. (C).
Kiton Red S. (C).
Kiton Red (C).
,, ,, 6B. (C).
Pure Bordeaux B. (C).
Roccelline (C).

Blacks, mordant with 3 per cent. hematine

Acid Black 4BNN. (G).
,, ,, HA. (C).
,, ,, PR. (C).
,, ,, PB. (C).
,, ,, (Ca).
Coomassie Black DW. (B).
Fast Sulphon Black F. (Sa).
Naphthalene Black 12B. (B).
,, ,, B. (B).
,, ,, BD. (B).
Naphthol Black ESN. (S).
Nigrosine G. Crystals (B).
,, B. Conc. (S).
,, ES. Crystals (S).
,, Crystals W. (Co).
,, S. (A).
,, B. (A).
,, A. (C).
,, B. (C).
,, K. (C).
,, S. 1471 (C).

Basic Dyes

Browns

Basic Brown BXN. (D).
,, ,, GX. (D).
,, ,, 1557 (C).
Bismarck Brown R. 100s. (B).
,, ,, G. (C).
,, ,, R. (C).
,, ,, M. (C).
,, ,, 8634 (S).
,, ,, (A).
,, ,, R. Conc. (H).
,, ,, R. (H).
,, ,, G. (H).
,, ,, R. Conc. (Co).
,, ,, Y. (Ca).
,, ,, R. (Ca).

Canelle 1352 (C).
,, 3373 (C).
,, 5733 (C).
,, 8337 (C).
,, 63N. (C).
,, OF. (C).
,, ES. (C).
Leather Brown A. (C).
,, ,, G. (C).
,, ,, 135 (C).
,, ,, 3378 (C).
,, ,, 4183 (C).
,, ,, 8669 (C).
Vesuvine GS. (Sa).
,, R. (Sa).

Yellows

Brilliant Phosphine G. (C).
,, ,, 2G. (C).
,, ,, 5G. (C).
,, ,, R. (C).
Patent Phosphine G. (C).
,, ,, 2G. (C).

Patent Phosphine M. (C).
,, ,, R. (C).
,, ,, GGMK.(C).
Saba Phosphine G. (Sa).
,, ,, 2G. (Sa).
Tannoflavine T. (Sa).

Blacks, mordant with 3 per cent. hematine

French Black 67445 (B).
Leather Black A. (Sa).
,, ,, CII. (C).

Leather Black SM. (C).
,, ,, CBD. (C).

Direct Dyes, dyed in a weak acetic acid bath

Browns

Chrome Leather Brown G. 98 (C).
Chrome Leather Brown R. 99 (C).
Chlorazol Brown G. (B).
Chlorazol Brown GN. Ex. (B).
Chlorazol Brown RN. Ex. (B).

Chlorazol Brown HX. (B).
Dianol Dark Brown BM. (B).
,, Brown GM. (B).
Diphenyl Brown GR. *supra* (G).
Omega Chrome Brown G. (Sa).
Omega Chrome Brown P. (Sa).

Yellows and Oranges

Afghan Yellow GX. (B).
Alizarine Yellow G. (Sa).
,, Orange R. (Sa).
Chlorazol Fast Yellow B. (B).
,, ,, R. (B).
,, ,, NX. (B).
,, ,, FG. (B).
,, Orange R. Ex. (B).

Chrysophenine G. (B).
Diphenyl Chlorine Yellow FF. (G).
Dianol Fast Orange G. (B).
Polyphenyl Yellow R. (G).
Polyphenyl Orange R. Ex. (G).
Sun Yellow 3G. (G).

Reds and Maroons

Benzo Purpurine 4B. (B).
Chicago Red (G).
Chlorazol Pink Y. (B).
Dianol Fast Red F. (B).

Dianol Fast Pink BK. (B).
,, Fast Red K. (B).
Diphenyl Fast Red B. (G).
Jasmine (G).

Greens and Blues

Brilliant Delphine Blue B. (Sa).
Chlorazol Sky Blue GW. (B).
,, ,, FF. (B).
,, Blue 3B. (B).
,, Green B. (B).
,, Dark Green PL. (B).

Chlorazol Dark Green PL. (B).
Diphenyl Deep Blue R. (G).
,, Green KGW., *supra* (G).
Diphenyl Blue KF. (G).
Fast Blue 3R. (Sa).
Gallocyanine (Sa).

Violets

Chlorazol Violet WBX. (B).

Dianol Violet R. (B).

Blacks

Dianol Black BH. (B).
Chlorazol Black E. Ex. (B).
,, ,, DV. (B).
Chrome Leather Deep Black G. Conc. (C).
Chrome Leather Deep Black C. Conc. (C).

Chrome Leather Black E. (C).
,, ,, E. Ex. (C).
Chrome Leather Black E. Ex. Conc. (C).

Mordant Dyestuffs

Yellows and Browns

Alizarine Orange M. Paste (B).
Alizarine Brown M. Paste (B).
Alizarine Yellow G. (Sa).
,, ,, R. (C).
Chrome Fast Yellow 2G. (C).
,, ,, 5G. (C).
Chrome Fast Brown A. (C).
,, ,, G. (C).
,, ,, PC. (C).
,, ,, R. (C).
,, ,, 537 (C).
Chrome Leather Brown 2G. (C).
Khaki Yellow WN. Paste (B).

APPENDIX D

THE DETERMINATION AND CONTROL OF ACIDITY IN TAN LIQUORS

W. R. ATKIN and F. C. THOMPSON

THE importance of the acidity of tan liquors is shown by the ample literature on the subject, describing for the most part work which has not achieved its aim, namely, the actual measurement of the swelling power of tan liquors. At the outset we may state our opinion that acidity, even when the presence of salts of weak acids is taken into account, is not the only factor governing swelling. Two factors, the influence of which is obscure, are : (*a*) the astringency and actual tanning effect of the tannins present, and (*b*) the effects of neutral salts of strong acids such as sodium chloride, sodium sulphate, etc. A well-conceived and direct method of arriving at the effect of astringency, etc., is that of Claflin, who carries out swelling experiments with hide-powder and the liquor under investigation, where the amount of liquid absorbed by the hide-powder measures the swelling power. The influence of neutral salts has been well brought out in numerous papers by J. A. Wilson and his collaborators, A. W. Thomas and M. E. Baldwin, and by J. W. McBain. The effect of adding sodium chloride to dilute hydrochloric acid is to raise the hydrion concentration as measured by the hydrogen electrode, whereas sodium sulphate added to weak acids has an opposite effect.

McBain found that the partial vapour pressure of acetic acid in dilute solution was greatly augmented in the presence of sodium chloride. These interesting effects are believed by Wilson to be intimately connected with the degree of hydration of the added ions, whereas McBain speaks of "enhanced chemical potential." Whatever the cause the effect is of great importance, particularly in chrome tanning.

In this paper, however, we are concerned only with a direct determination of acidity. All previous attempts have depended upon titration of the tan liquors with alkali. H. R. Procter and R. A. Seymour-Jones published in 1910 a comprehensive review of the earlier work on this subject, and in addition described several variations involving the use of indicators. The two main difficulties, however, were :

(*a*) The colour of the tan liquors masked the colour of the indicator ;

(*b*) Except in a neutral atmosphere there was always a considerable oxidation and darkening on the addition of alkali.

Attempts have been made to overcome the first difficulty by detannisation previous to titration, but this procedure causes serious errors, as in almost all cases there is a marked co-precipitation of acid. This objection applies to the present official method of the A.L.C.A., in which detannisation is effected by means of an alcoholic solution of gelatine. Stiasny, however, detannises with a mixture of hydrochloric acid and formaldehyde, and in this case there appears to be no loss of acid, but the method can only be applied to catechol tans.

The question now to be discussed is what acidity should be measured. It is necessary to define at the outset what is meant by " acidity," and to show that measurement of total content in acid, even if this could be accurately performed, would not give the information which is desired by the sole leather tanner. A concrete example may make this point clear. Consider the two following cases : (*a*) 25 c.c. of $N/10$ acetic acid, and (*b*) 25 c.c. of $N/10$ acetic acid containing 0·205 grm. of sodium acetate, and consequently also $N/10$ in this substance. If these two solutions were titrated with alkali, using phenolphthalein as indicator, the same result would be obtained in each case, but if an attempt were made to titrate, using methyl orange, it would be found that mixture (*b*) was already alkaline. In harmony with this, the swelling power on water-swollen gelatin of solution (*b*) would be nil, whereas (*a*) would produce a pronounced increase of swelling. The explanation is found in a consideration of the ionisation phenomena in the two cases.

As is well known, the property of acidity is due to the presence in solution of hydrogen ions. An acid in solution dissociates into ions according to the following scheme :

$$HAc \rightarrow H^{\cdot} + Ac'.$$

In the case of weak acids the extent of this dissociation, *i.e.* the concentration of ions produced, is in accordance with the well-known law of mass-action.

This states that under given circumstances of original concentration and temperature the concentrations of the products of reactions at equilibrium are, when multiplied together, in strict proportion to the concentrations of reacting substances, also multiplied together. In other words, if A and B react together to form X and Y, then at equilibrium $[A] \times [B] = K[X] \times [Y]$.

The square brackets indicate *concentrations*, and K is a number termed the equilibrium constant of the reaction.

Consider from this point of view the electrolytic dissociation or ionisation of a weak acid, *i.e.* one which is only ionised to a slight extent. Here we only have *one* reacting substance, namely, the acid which is partially split up into the *two* reaction products, the kation $(H\cdot)$ and the anion (Ac')—

$$K[HAc] = [H\cdot] \times [Ac'].$$

Here K is the dissociation or ionisation constant, and in the case of weak acids is always very small, *e.g.* 0·000018 for acetic acid. The square brackets indicate concentration in terms of normality, *i.e.* for $N/10$ acetic acid, of which over 98 per cent. remains undissociated, $[HAc] = 0{\cdot}1$, approximately, being actually a little less.

Whatever other ions may be present in solution at the same time as those of acetic acid, the above equation holds good. Consequently, if the concentration of the anion $[Ac']$ be increased by some means without increasing the concentration of undissociated acid $[HAc]$, then in order to maintain the equality the concentration of the kation $[H\cdot]$ must diminish. In other words, the acidity is diminished. In the case of decinormal acetic acid we have

$$K[CH_3COOH] = [H\cdot] \times [CH_3COO'] = [H\cdot]^2,$$

since hydrogen and acetate ions are necessarily equal in number. Since the acid is decinormal and almost all undissociated, we have approximately

$$0{\cdot}1K = [H\cdot]^2$$

or

$$[H\cdot] = \sqrt{0{\cdot}0000018}$$

$$= 0{\cdot}00134 = 1{\cdot}34 \times 10^{-3}.$$

The effect of adding sodium acetate is to increase largely the number of acetate ions. Usually the salt of even a weak acid is largely dissociated, and in extending the calculation to the case of mixture (*b*) we shall assume as an approximation that sodium acetate is completely ionised in decinormal solution. Thus $[Ac']$ now $= 0{\cdot}1$, whilst $[HAc]$ is unaffected. The sodium ions produced do not affect the case. We still have

$$K[CH_3COOH] = [H\cdot] \times [CH_3COO'],$$

but now

$$0{\cdot}1\ K = [H\cdot] \times 0{\cdot}1$$

or

$$[H\cdot] = K = {\cdot}000018 = 1{\cdot}8 \times 10^{-5}.$$

Thus [H·], or the acidity, has been reduced to less than 2 per cent. of its value in *N*/10 acetic acid. The effect of any other amount of sodium acetate can be calculated easily. Suppose the *N*/10 acid to be made *N*/1 in sodium acetate. Then approximately

$$0{\cdot}1\ \mathrm{K}=[\mathrm{H}\cdot]\times 1{\cdot}0$$

or

$$[\mathrm{H}]=\frac{\mathrm{K}}{10}\quad\text{or}\quad 1{\cdot}8\times 10^{-6}.$$

More accurate results can be obtained by finding the actual percentage dissociation of sodium acetate from the tables and using it in the calculation.

An interesting and important property of mixtures of weak acids and their salts is that the [H·] is very little altered by even considerable dilution. Such solutions are called "buffers," and their behaviour is readily explained in the light of the above equations. Consider again the case of mixture (*b*). We have here

$$0{\cdot}1\mathrm{K}=[\mathrm{H}\cdot]\times 0{\cdot}1.$$

This formula may now be made more accurate by introducing corrections for the not quite complete ionisation of the sodium acetate, which in *N*/10 solution is ionised to the extent of 79 per cent. and in *N*/100 solution to 87 per cent.

Consequently, for the *N*/10 solution the above equation becomes

$$0{\cdot}1\times\mathrm{K}=[\mathrm{H}\cdot]\times 0{\cdot}1\times\frac{79}{100},$$

or

$$0{\cdot}1\times 1{\cdot}8\times 10^{-5}=[\mathrm{H}\cdot]\times 0{\cdot}079$$

or

$$[\mathrm{H}\cdot]=2{\cdot}28\times 10^{-5}.$$

Now consider the case where mixture (*b*) is diluted ten times. We now have

$$0{\cdot}01\times\mathrm{K}=[\mathrm{H}\cdot]\times 0{\cdot}01\times\frac{87}{100},$$

or

$$0{\cdot}01\times 1{\cdot}8\times 10^{-5}=[\mathrm{H}\cdot]\times 0{\cdot}0087$$

or

$$[\mathrm{H}\cdot]=2{\cdot}07\times 10^{-5}.$$

In the case of pure acetic acid containing no added sodium acetate the [H·] is $1{\cdot}3\times 10^{-3}$ in *N*/10 solution and $0{\cdot}42\times 10^{-3}$ in N/100 solution, representing a drop of nearly 70 per cent., as compared with about 10 per cent. in the case of mixture (*b*).

Now consider the case of pure distilled water which is very slightly ionised into hydrions and hydroxyl ions so that

$$\mathrm{K}[\mathrm{H_2O}]=[\mathrm{H}\cdot]\times[\mathrm{OH}']\quad\text{and}\quad[\mathrm{H}\cdot]=[\mathrm{OH}'].$$

As the mass of undissociated water is very large compared with the mass of the free ions we might regard it as also constant, so $[H\cdot] \times [OH'] = Kw$.

Here Kw is the dissociation constant for pure water, and has the very low value at 21° C. of 10^{-14}, and thus the value for $[H\cdot]$ or $[OH']$ is 10^{-7} grm. ions per litre.

If an acid be added to distilled water the acid is dissociated either partially or wholly into hydrions and the anions of the acid employed. Thus $[H\cdot]$ in such a mixture is greater than 10^{-7}, and the solution is "acid." Suppose acid had been added so that $[H\cdot]$ was 10^{-3}, then $[OH']$ would be 10^{-11}, for

$$[H\cdot] \times [OH'] = 10^{-14}.$$

From the above it will be understood that a solution is "neutral," "acid," or "alkaline" according to whether $[H\cdot]$ has a value equal to, greater than, or less than 10^{-7} respectively. Obviously, if $[H\cdot]$ does not equal 10^{-7}, then it cannot be equal to $[OH']$.

Sörensen, in order to facilitate the plotting of curves, has introduced the symbol P_H to denote what he calls the "hydrogen ion exponent," where P_H is the logarithm to the base 10 of $[H\cdot]$ but with the negative sign omitted, or $P_H = -\log_{10} [H\cdot]$. For example, $N/10$ acetic acid has $[H\cdot] = 1{\cdot}36 \times 10^{-3} = 10^{0{\cdot}133} \times 10^{-3} = 10^{-2{\cdot}867}$, so $P_H = 2{\cdot}867$.

It should be noticed that P_H decreases with increasing acidity, and that if $[H\cdot]$ be increased tenfold the value of P_H is decreased by 1·0.

From the case of acetic acid and sodium acetate mentioned above it will be seen that P_H cannot be determined by ordinary titration.

The most accurate method of determining the $[H\cdot]$ or P_H is by means of the hydrogen electrode, and this method has been applied by Wood, Sand, and Law in the case of tan liquors. The method is an electrical one, requiring a considerable amount of apparatus, and does not seem to have become universally popular with tannery chemists.

Other methods depend upon the measurement of the velocity of chemical reactions, such as the hydrolysis of cane sugar or methyl acetate, where acids are used as catalysts, but these involve too much time. The simplest method is by the use of indicators, and may be called the colorimetric method. It has the great advantage that it is rapid, and does not require any elaborate apparatus.

As is well known, indicators are substances that vary in colour with varying acidity or alkalinity of the solution to which they are added. This change of colour takes place over a definite range of P_H, and at various points within this range the indicator shows intermediate tints. The solution is "neutral" to the indicator at the mid point of the range. This neutrality does not mean that $[H\cdot]=[OH']$ as in pure water. For example, "neutrality" to phenolphthalein occurs about $P_H=9$, whilst in the case of methyl orange "neutrality" is in the region $P_H=4$, the $[H\cdot]$ in the latter case being 100,000 times greater than in the case of phenolphthalein. Litmus, however, has its "neutral" point at about 6·6 and brom-thymol blue at about 6·8. Table I. shows a list of convenient indicators, many of which are of the new sulphone phthalein type described by Mansfield Clark, Lubs, and Acree. One of them, thymol blue, it will be noticed, has a double change, one in fairly strong acid solution, and the other like that of phenolphthalein.

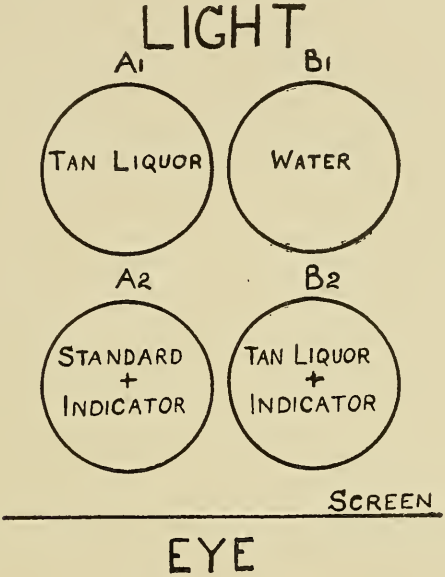
The colorimetric method has been described by various workers, including Veley and Sörensen, but the results obtained were only rough in the case of coloured fluids. Sörensen also pointed out that the presence of proteins vitiated the results with certain indicators. This was especially the case with colloid indicators such as Congo red. Walpole surmounted the difficulties due to the colour of the fluids by matching the solution under investigation (which contained the indicator) against a colourless solution of standard P_H containing the same amount of indicator observed through a layer of the coloured fluid. His method was modified by Hurwitz, Meyer, and Osterberg, who used test-tubes held in a box, and finally by Cole and Onslow, who have further improved this latter device, which is termed a "comparator," by the addition of a ground-glass plate, as shown in the diagram (p. 663). For determining the acidity of tan liquors a comparator which takes two pairs of tubes is as large as is necessary. The method of procedure is as follows :—

Test-tube A_1 contains 10 c.c. of filtered tan liquor, A_2 contains 10 c.c. of a solution of standard P_H together with five or ten drops of a suitable indicator, *i.e.* an indicator which is changing its shade distinctly in that region of acidity. Test-tube B_1 contains distilled water, and B_2 10 c.c. of filtered tan liquor and the same number of drops of indicator solution as in A_2. If on looking through the two pairs of tubes the colours match, then the P_H of the tan liquor is that of the standard used in A_2. If not, other standards of deeper or lighter shade as may be required are substituted for that in A_2. The matching is usually performed in a minute or so, provided that the necessary ranges of standards are to hand. The test-tubes must be of colourless glass, and of the same diameter. A selection can easily be made by pipetting

TABLE I.

Indicator.	Chemical Name.	Range of P_H.	Colour Change Acid-alkaline.	Strength of Solution.
Methyl violet	..	0·1– 3·2	green-blue	0·02 per cent.
Thymol blue	Thymol sulphone phthalein	1·2– 2·8	red-yellow	0·04 ,,
Brom-phenol blue	Tetra-brom-phenol sulphone phthalein	2·8– 4·6	yellow-blue	0·04 ,,
Methyl orange	*p*-Dimethyl amino azobenzene sulphonic acid	3·1– 4·4	red-yellow	0·01 ,,
Methyl red	*p*-Dimethyl amino azobenzene *o*-carboxylic acid	4·4– 6·0	red-yellow	0·02 per cent. in 60 per cent. alcohol.
Brom-cresol purple	dibrom-*o*-cresol sulphone phthalein	5·2– 6·8	yellow-purple	0·04 per cent.
Brom-thymol blue	dibrom-thymol sulphone phthalein	6·0– 7·6	yellow-blue	0·04 ,,
Phenol red	phenol sulphone phthalein	6·8– 8·4	yellow-red	0·02 ,,
Cresol red	*o*-cresol sulphone phthalein	7·2– 8·8	yellow-red	0·02 ,,
Thymol blue	thymol sulphone phthalein	8·0– 9·6	yellow-blue	0·04 ,,
Phenolphthalein	..	8·3–10·0	colourless-red	0·05 per cent. in 50 per cent. alcohol.

10 c.c. of water into a number of, say, $\frac{5}{8}$-inch tubes, which are very convenient, and using those which give the same level of water. The tubes are best divided thus into sets, marked, and kept separately in boxes. The most convenient means of obtaining drops of indicator solution of equal size is to use the slow-dropping Dreyer pipettes, which have a capillary end about 1 inch long. With these pipettes there is no danger of adding too many drops accidentally. As a source of light a Nernst lamp proved to be excellent, and good results were obtained with an inverted incandescent gas mantle and with an electric lamp of the half-watt type.



Tan liquors have acidities which lie as a rule between $P_H=3{\cdot}0$ and $P_H=4{\cdot}5$. Exceptions are often found in the case of synthetic tannins, which may be so acid as to reach $P_H=1{\cdot}5$. It must first be emphasised that neutrality from the tanner's point of view is the point of minimum swelling, and that this is *not* when $P_H=7$, *i.e.* when $[H^{\cdot}]=[OH']$. Experiments by Procter, Loeb, Michaelis, and by the authors all tend to fix the isoelectric point of gelatin, or the point of minimum swelling, at $P_H=4{\cdot}5\text{–}4{\cdot}7$.

The determination of the point of minimum swelling gives us one limit for the range of P_H in the acid standards. It is plainly not necessary to go nearer to neutrality than $P_H=4{\cdot}7$. The other limit may be taken as $P_H=2{\cdot}8$ for most purposes. Only synthetic or treated tannins are likely to lie outside this range. The standards used were mixtures of (1) acetic acid and sodium acetate, (2) acid potassium phthalate and hydrochloric acid. The best indicator appears to be tetra-brom-phenol-sulphone-phthalein or brom-phenol blue. The colour of this indicator changes continuously from $P_H=2{\cdot}8$ to $P_H=4{\cdot}6$, though not very much near the limits. Brom-phenol blue, however, is dichroic, and is best observed through a yellow colour screen which cuts off blue rays. A convenient mode of making such a screen is to paint transparent parchment with a mixture of 0·6 per cent. solution of phenol red and *M*/5 solution of potassium dihydrogen phosphate (27·23 grams/liter). The preparation of the standards is a very simple matter, following the tables given. The solutions required are *N*/5 acetic acid, *N*/5 sodium acetate prepared by neutralising 200 c.c. *N*/1 caustic soda with *N*/1 acetic acid and diluting to 1 liter, *M*/5 acid potassium phthalate (40·828 grams/liter), *N*/5 caustic soda, and *N*/5 hydrochloric acid:—

STANDARD P_H SOLUTIONS.

SERIES I.

50 c.c. *M*/5 acid potassium phthalate ; *x* c.c. *N*/5HCl, mixed and diluted to 200 c.c.

P_H.	*x*.	P_H.	*x*.	P_H.	*x*.
2·8	26·42	3·2	14·70	3·6	5·97
2·9	22·80	3·3	11·80	3·7	4·30
3·0	20·32	3·4	9·90	3·8	2·63
3·1	17·70	3·5	7·50	3·9	1·00

SERIES II.

50 c.c. *M*/5 acid potassium phthalate ; *x* c.c. *N*/5NaOH, mixed and diluted to 200 c.c.

P_H.	*x*.	P_H.	*x*.
4·0	0·40	4·4	7·50
4·1	2·20	4·5	9·60
4·2	3·70	4·6	12·15
4·3	5·17		

SERIES III.

x c.c. $N/5$ sodium acetate $+ 100 - x$ c.c. $N/5$ acetic acid.

P_H.	x.	$100 - x$.	P_H.	x.	$100 - x$.
3·8	12	88	4·3	31	69
3·9	15	85	4·4	37	63
4·0	18	82	4·5	42·5	57·5
4·1	22	78	4·6	48	52
4·2	26·5	73·5	4·7	54	46

For instance, a solution of $P_H = 3{\cdot}8$ may be prepared in either of the two following ways: (*a*) 50 c.c. $M/5$ phthalate $+ 2{\cdot}63$ c.c. $N/5$ hydrochloric acid diluted to 200 c.c., or (*b*) 12 c.c. $N/5$ sodium acetate $+ 88$ c.c. $N/5$ acetic acid; 10 c.c. of either of these solutions, together with five drops of brom-phenol blue solution, is pipetted into a test-tube, corked well, and labelled $P_H = 3{\cdot}8$. It will be found convenient when working in the range from $P_H = 2{\cdot}8$ to $P_H = 3{\cdot}7$ to use ten drops of indicator solution in order to intensify the colour differences. The whole range required should be made up and kept in a test-tube stand, preferably in the dark. The authors have found that the colours do not change appreciably in the course of a month. These sets of standards have been worked out by Clark and Lubs, and have been standardised against the hydrogen electrode.

A number of tannin solutions have been examined, both in the above way and by Procter's lime-water method, with the following results, which have been arranged in order of increasing acidity:—

Tan Liquor.	Procter lime-water method c.c. satd. lime-water per 10 c.c. tan liquor.	Colorimetric Method.	
		P_H.	$[H^{\cdot}]$ as normality.
No. 1 . .	1·8	4·3	5×10^{-5}
,, 2 . .	5·6	4·2	$6{\cdot}3 \times 10^{-5}$
,, 3 . .	6·2	4·1	8×10^{-5}
,, 4 . .	6·8	4·1	8×10^{-5}
,, 5 . .	16·2	3·8	$1{\cdot}6 \times 10^{-4}$
,, 6 . .	17·3	3·7	2×10^{-4}
,, 7 . .	27·9	3·4	4×10^{-4}
,, 8 . .	34·5	3·1	8×10^{-4}

It will be noticed that the lime-water figures are in the same order as the acidities, though no exact correspondence is revealed. There is no necessary connection between P_H and the lime-water figure.

If it be required to raise the acidity of a tan liquor, this can easily be done by titrating the liquor with a standard solution of the acid to be used until its acidity reaches the required P_H as shown in the comparator; a calculation will then show how much commercial acid should be added to the liquor in the pit. What, however, is a desirable P_H must be fixed by the tanner according to the class of leather he is dealing with. The best way is to note carefully the acidities of liquors which he finds satisfactory, and to reproduce these as required. It will be obvious that acid is titrated by acid; no alkali is used, and the difficulties due to oxidation and darkening entirely disappear.

An interesting application of this acidity method is in the case of freshly made analytical solutions of tannin. A surprising variation in acidity was found, the range being almost as great as in used liquors.

Tanning Material.	RANGE OF P_H.
Solid mimosa extract (4 samples)	4·1–4·3
Sumach (4 samples)	4·1–4·2
Liquid myrobalan extract (3 samples)	3·3–3·4
Solid quebracho extract (2 samples)	4·1
Liquid quebracho extract (3 samples)	4·0–4·2
Solid chestnut extract (1 sample)	3·5
Liquid chestnut extract (2 samples)	3·7–3·75

Wood, Sand, and Law have previously determined the acidity of tan liquors directly by the hydrogen electrode, which is the standard method, and much more accurate than the method described in this paper. However, it has not become popular with tannery chemists, and our purpose is to give a method which whilst sufficiently accurate is yet simple in execution and easy to understand. The electrometric method is no doubt easily and quickly carried out when the complicated apparatus is once set up, but to understand and appreciate the method of working requires a considerable acquaintance with difficult thermodynamic theory. Once the standard buffer mixtures described above (without indicator) have been prepared, it will be found convenient to keep them in well stoppered and carefully labelled bottles. Thus new colour standards may be quickly prepared by adding the indicator to 10 c.c. when needed.

APPENDIX E

THE CAUSTIC ALKALINITY OF LIME LIQUORS

William R. Atkin and John Atkin, M.C.

In a recent publication by one of us a method was described for ascertaining the caustic alkalinity of lime liquors, but the method so described was indirect, and involved four separate determinations. We have present in lime liquors the following substances which constitute alkalinity :—

(*a*) Calcium hydroxide.
(*b*) Sodium hydroxide.
(*c*) Sulphydrates of sodium and calcium.
(*d*) Ammonia and, perhaps, amines, but these latter are present, if at all, in very small amounts, and may be ignored for practical purposes.
(*e*) Sodium and calcium salts of the various protein decomposition products, such as proteoses, peptones, amino acids, and fatty acids, produced from amino acids by deaminisation.

In order to maintain uniformity with our earlier paper on this subject the letters (*a*), (*b*), (*c*), (*d*), and (*e*) are employed to refer to calcium hydroxide, sodium hydroxide, etc., as above, so that $a+b$ is the caustic alkalinity. In addition all estimations are performed on 25 c.c. portions of the filtered lime liquor, and results stated in c.c. $N/10$ acid or alkali.

Several methods have been suggested for ascertaining the caustic alkalinity directly by one titration, but they proved of little value owing to the difficulty of choosing a suitable indicator.

We have in lime liquors two strong bases, sodium and calcium hydroxides, together with a weak base, ammonium hydroxide, and the salt of a strong base combined with a weak acid (sodium sulphydrate, which is formed from the sodium sulphide used for sharpening the lime liquors). It is well known that indicators such as phenolphthalein, which have a colour change on the alkaline side of true neutrality, cannot be used for the accurate titration of ammonia solutions. On the other hand, an indicator such as methyl orange, which possesses a colour change well on the acid side of true neutrality, would cause to be included in the titration not only the caustic alkalinity but all the ammonia, hydrosulphide, and also the sodium and calcium salts of the decomposition products of the dissolved proteins, and, as Bennett points out, this titration with methyl orange estimates the total alkalinity. However, by the aid of the ionic theory, and the employment of the comparator recently described, it has been found possible to determine quickly, and with reasonable accuracy, the caustic alkalinity of lime liquors. Consider the case of ammonium hydroxide, which is a weak base, and therefore is only slightly dissociated into ions in aqueous solution,

$$NH_4OH \rightarrow NH_4\cdot + OH'.$$

By the law of mass action we have

$$K = \frac{[NH_4\cdot]\,[OH']}{[NH_4OH]} \quad . \quad . \quad . \quad (1)$$

where K is a constant known as the dissociation constant, and at 25° C. has a value of $2{\cdot}3 \times 10^{-5}$. $[NH_4\cdot]$ denotes the concentration of ammonium ions, $[OH']$ the concentration of hydroxyl ions, and $[NH_4OH]$ is the concentration of the undissociated ammonium hydroxide. As $[NH_4\cdot]$ or $[OH']$ is relatively very small compared with $[NH_4OH]$, we may regard the latter as constant, so that the above equation may be simplified to

$$[NH_4\cdot] \times [OH'] = \text{constant} \quad . \quad . \quad . \quad (2)$$

If, now, a considerable quantity of $NH_4\cdot$ ion be added to a solution of ammonia as an ammonium salt, *e.g.* ammonium chloride, which is almost completely ionised in dilute solution, we have $[NH_4\cdot]$ considerably increased, but as the product $[NH_4\cdot] \times [OH']$ must remain constant, it follows that $[OH']$ must be correspondingly decreased.

This reasoning is exactly analogous to that of the case of acetic acid and sodium acetate, discussed on p. 658, except that in this latter case the $[H\cdot]$ is considerably decreased by the addition of sodium acetate to the weak acetic acid. Michaelis has calculated the $[OH']$ of various mixtures of ammonium hydroxide and ammonium chloride, which are given in the following table. At 18° C. however

$$[H\cdot] \times [OH'] = 0{\cdot}64 \times 10^{-14},$$

so that knowing $[OH']$ it is possible to calculate $[H\cdot]$. For curve plotting the symbol P_H, which is $-\log_{10}\,[H\cdot]$, is used, therefore both $[H\cdot]$ and P_H values are appended to Michaelis' figures.

TABLE

Calculated figures by Michaelis showing [OH′] of various mixtures of ammonium hydroxide and ammonium chloride, and also the corresponding [H·] and P_H values.

Ratio. $NH_4OH : NH_4Cl$.	Per cent. *N*/10 NH_4OH.	Per cent. *N*/10 NH_4Cl.	[OH′].	[H·].	P_H.
32 : 1	96·7	3·3	$6{\cdot}4\times10^{-4}$	1×10^{-11}	11·0
16 : 1	94·1	5·9	$3{\cdot}2\times10^{-4}$	2×10^{-11}	10·7
8 : 1	88·9	11·1	$1{\cdot}6\times10^{-4}$	4×10^{-11}	10·4
4 : 1	80·0	20·0	8×10^{-5}	8×10^{-11}	10·1
2 : 1	66·7	33·3	4×10^{-5}	$1{\cdot}6\times10^{-10}$	9·8
1 : 1	50·0	50·0	2×10^{-5}	$3{\cdot}2\times10^{-10}$	9·5
1 : 2	33·3	66·7	1×10^{-5}	$6{\cdot}4\times10^{-10}$	9·2
1 : 4	20·0	80·0	5×10^{-6}	$1{\cdot}3\times10^{-9}$	8·9
1 : 8	11·1	88·9	$2{\cdot}5\times10^{-6}$	$2{\cdot}6\times10^{-9}$	8·6
1 : 16	5·9	94·1	$1{\cdot}2\times10^{-6}$	$5{\cdot}2\times10^{-9}$	8·3
1 : 32	3·3	96·7	6×10^{-7}	1×10^{-8}	8·0

It must be pointed out that dilution has little influence on the (OH′) of mixtures of ammonium hydroxide and ammonium chloride, as it is really the ratio $\frac{[NH_4OH]}{[NH_4\cdot]}$ that is the deciding factor, as will be seen by re-writing equation (1) in the form

$$[OH'] = \frac{K\times[NH_4OH]}{[NH_4\cdot]} \quad . \quad . \quad . \quad (3)$$

Thus from the table and curve it follows that a mixture of equal parts of ammonium hydroxide and ammonium chloride has

$$[OH'] = 2\times10^{-5},$$

corresponding to a P_H value of 9·5.

Now, consider what happens when a solution of ammonia is titrated with standard acid, using phenolphthalein as indicator. Phenolphthalein has a range of colour change from $P_H = 8{\cdot}3$ (colourless) to $P_H = 10{\cdot}0$ (deep red). Thus at $P_H = 8{\cdot}3$ ammonia is 94 per cent. neutralised, whereas at $P_H = 10{\cdot}0$ it is only 24 per cent. neutralised.

Not only have we to consider the ammonia, however, but Stiasny's results seem to suggest that the presence of calcium salts might have a profound influence on the [OH′], owing to the formation of complex calcium-ammonia ions, but experiments carried out on the following lines proved conclusively that calcium salts do not alter the [OH′] of mixtures of ammonia and ammonium chloride to any appreciable extent.

Various mixtures of *N*/10 ammonia and *N*/10 ammonium chloride were made up and the P_H determined exactly as in the manner recently described for the determination of acidity in tan liquors (*loc. cit.*), except that, of course, a different indicator (phenolphthalein) and different standards were used. These standards were made up according to the instructions given by Cole. The actual values of P_H obtained were found to agree very well with the calculated figures of Michaelis.

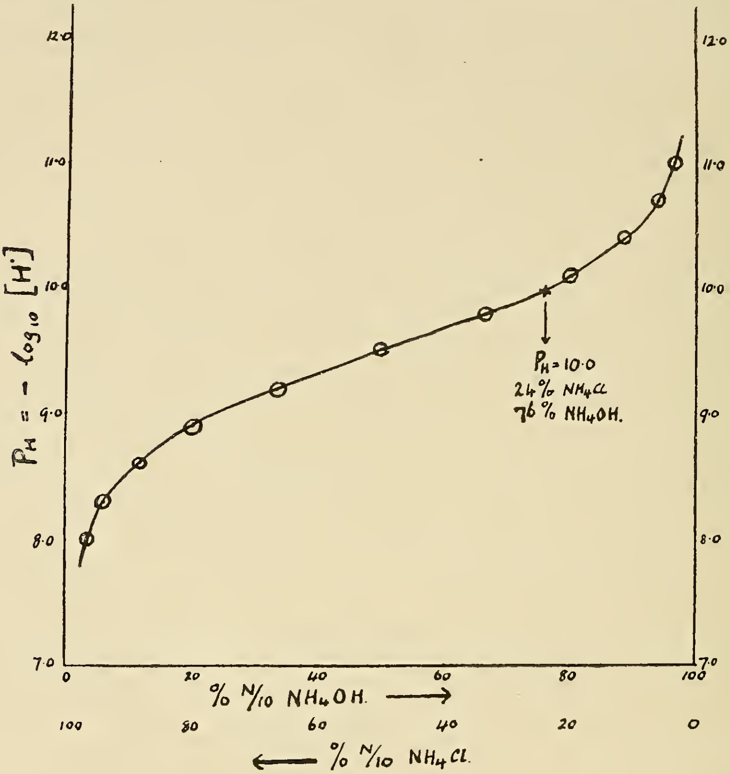


FIG. 130.

The P_H values of various mixtures of ammonia and ammonium chloride to which varying quantities of *N*/5 calcium chloride or *N*/10 sodium chloride had been added were determined as shown in the table on next page.

From these results it will be obvious that calcium salts do not cause any appreciable differences in the P_H, and therefore in

Mixture consisting of					
c.c. $N/10$ NH_4OH.	c.c. $N/10$ NH_4Cl.	c.c. distilled water.	c.c. $N/10$ NaCl.	c.c. $N/5$ $CaCl_2$.	P_H observed.
5	5	10	..	..	9·45
5	5	..	..	10	9·45
5	5	..	10	..	9·45
3·9	6·1	10	..	..	9·3
3·9	6·1	..	..	10	9·3

[OH′], so that on titrating a lime liquor with $N/10$ HCl the calcium or sodium chlorides so formed will not affect the [OH′] of the ammonium hydroxide.

The effect of hydrosulphides must now be considered. Sodium sulphide is hydrolytically dissociated in solution as follows :

$$Na_2S + H_2O \rightarrow NaOH + NaSH.$$

The caustic soda of course forms part of the caustic alkalinity, but sodium sulphydrate is also hydrolysed to some extent in aqueous solution.

Walker found experimentally that $N/10$ NaSH was hydrolysed to the extent of 0·14 per cent. :

$$NaSH + H_2O \rightarrow NaOH + H_2S,$$

whence $$[OH'] = {\cdot}0014 \times 0{\cdot}1$$
$$= {\cdot}00014, \text{ or } 1{\cdot}4 \times 10^{-4} \text{ grm.-mols. per liter.}$$

Knowing the dissociation constant of H_2S, which is a very weak acid, it is possible to calculate the [OH′] of $N/10$ NaSH.

We have $NaSH + H_2O = NaOH + H_2S$.

If, therefore, we have 1 mol. of NaSH in "v" liters of water, and of this a fraction "x" is hydrolysed, it has been shown that

$$x = \sqrt{\frac{v \times Kw}{ka}},$$

where Kw is the dissociation constant of water (at 25° C. $Kw = 1{\cdot}2 \times 10^{-14}$) and ka is the dissociation constant of H_2S ($ka = 5{\cdot}7 \times 10^{-8}$ at 25° C.), so by substituting these values in the above equation and putting

$$v = 10 \text{ (for decinormal NaSH)},$$

we have $$x = \sqrt{\frac{10 \times 1{\cdot}2 \times 10^{-14}}{5{\cdot}7 \times 10^{-8}}} = 1{\cdot}45 \times 10^{-3},$$

or the concentration of NaOH, and consequently of the OH′ ion, is $1{\cdot}45 \times 10^{-3}$ mols. in 10 liters, or [OH′] is $1{\cdot}45 \times 10^{-4}$ normal, a result that agrees with Walker's experimental figures.

Now, in practice lime liquors are seldom used with a higher concentration of sulphide than corresponds to $N/20$ in sodium sulphydrate.

If we substitute $v=20$ in the above equation, we then have

$$x=\sqrt{\frac{20\times 1{\cdot}2\times 10^{-14}}{5{\cdot}7\times 10^{-8}}}=2{\cdot}05\times 10^{-3}$$

or

$$[\mathrm{OH}^1]=2{\cdot}05\times 10^{-3}\times 0{\cdot}05$$
$$=1{\cdot}025\times 10^{-4}\text{ normal,}$$

which at 25° C. corresponds to [H·] of $1{\cdot}15\times 10^{-10}$, or a P_H value of 9·93, *i.e.* practically $P_H=10{\cdot}0$.

From the above it is clear that if a lime liquor be titrated to a point corresponding to $P_H=10{\cdot}0$ the sodium and calcium hydroxides will be practically completely neutralised, the ammonia will be neutralised to the extent of 24 per cent. (see curve), but the sulphydrate will not have been affected. Thus the titration will be a measure of $a+b+0{\cdot}24$d. It is worthy of note that in all titrations to $P_H=10{\cdot}0$ no smell of escaping H_2S was detected, but if the titrations were carried beyond this point the smell of H_2S became quite distinct.

Hence by estimating the ammonia, preferably by distillation *in vacuo*, as described by Thompson and Suzuki, the value of $a+b$ (the caustic alkalinity) may be obtained from two determinations instead of four, as described in our earlier paper.

The choice of indicator in order to titrate to a P_H value of 10·0 is important. Phenolphthalein has a range of colour change from 8·3 to 10·0, and at the latter value it is coloured deep red. As a general rule an indicator is not suitable near the limits of the colour change, so that the most suitable indicator for our purpose appears to be thymolphthalein, which changes from colourless to blue over the range of P_H 9·3 to 10·5. Thus at $P_H=10{\cdot}0$ we are near the middle point of the colour change.

The titration to a value of $P_H=10{\cdot}0$ was carried out in the comparator previously described (*loc. cit.*), using boiling tubes (6 inches by 1 inch) of the same internal diameter as shown in the diagram (p. 673).

$N/10$ HCl was run slowly into tube B_2, stirring continuously, and when the match was nearly complete distilled water added until the total volume in B_2 was nearly 50 c.c. (It is convenient to scratch a mark on the boiling tubes corresponding to a capacity of 50 c.c.) The titration was continued until the colour seen through the tubes A_1 and A_2 matched that seen through B_1 and B_2.

It was noted that the blue colour of the thymolphthalein indicator faded after some time, so it is better to make up tube A_2 each time that a titration is being carried out.

LIGHT

A_1	B_1
25 c.c. lime liquor +25 c.c. distilled water.	50 c.c. distilled water.
A_2	B_2
50 c.c. solution of standard alkalinity $P_H=10{\cdot}0$. 10 drops of thymolphthalein solution.	25 c.c. lime liquor +10 drops thymolphthalein solution.

Ground glass screen————————————————

EYE

As the standard solution of $P_H=10{\cdot}0$, a mixture of 76 per cent. $N/10$ NH_4OH and 24 per cent. $N/10$ NH_4Cl was used. A liter of solution of this composition may be made up and kept in a stoppered bottle, the thymolphthalein being added to 50 c.c. as required.

Determinations of the caustic alkalinities of four lime liquors were made, and these results compared with results obtained by the method previously described. All titrations are given in terms of c.c. $N/10$ acid or alkali per 25 c.c. of filtered lime liquor.

	No. of Lime Liquor	1	2	3	4
Method described in this paper.	Titration to $P_H=10{\cdot}0$ $(a+b+0{\cdot}24d.)$	10·2	16·45	16·8	17·05
	Ammonia (*d*)	0·1	12·1	4·8	7·0
	0·24d.	·02	2·9	1·15	1·7
	∴ $a+b$ (caustic alkalinity)	10·18	13·55	15·65	15·35
Method of Atkin and Palmer.	1st H . CHO titration ($a+b+c-$amino acids)	9·1	13·3	19·9	18·9
	2nd H . CHO titration ($d+$amino acids)	1·1	12·6	5·0	7·35
	Ammonia (*d*)	0·1	12·1	4·8	7·0
	Sulphide (*c*)	0·0	0·6	4·4	3·7
	∴ $a+b$ (caustic alkalinity)	10·1	13·2	15·7	15·55

It will thus be seen that the agreement between the two methods is quite satisfactory.

INDEX

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