THE DYEING OF TEXTILE FABRICS

J. J. HUMMEL F.C.S.

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MANUALS OF TECHNOLOGY.

EDITED BY

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THE DYEING
OF
TEXTILE FABRICS.

BY

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YORKSHIRE COLLEGE, LEEDS.

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CLOTHWORKERS OF THE CITY OF LONDON,

AMONG THE EARLIEST AND MOST MUNIFICENT PATRONS

OF

TECHNICAL EDUCATION IN ENGLAND,

THIS WORK

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BY THE AUTHOR.

PREFACE.

The object of this Manual is to provide the teacher and student of Dyeing with a useful text-book giving exact scientific and practical information. It is intended also to supply the Dyer with explanations of the scientific principles involved in the operations of his art, in order that he may take a more intelligent interest in his work, and be stimulated to criticise it, and to determine, by means of well-devised experiments, whether his methods are rational and incapable of improvement, or the reverse.

Certain details have been furnished relating to the mode of applying the various Colouring Matters and Mordants, but these must not be regarded as fixed and unchangeable receipts, but rather as starting-points for further experimental work.

The Art of Dyeing being a special branch of Chemical Technology, no apology is offered for leavening the work with a wholesome amount of chemistry. The Dyer is specially urged to make himself acquainted with the general principles of chemical science, for assuredly the more such knowledge is brought to bear upon every detail of the art, the more rapid will be its progress.

It seemed necessary to give the somewhat complex chemical symbols and scientific names of the Coal-Tar colours in order to identify them, since, in the course of time, many of the present commercial names may be replaced by others, or applied to colouring matters not yet introduced. The advanced student will find them useful, for they show at a glance the chemical relationships.

existing between colours which possess similar dyeing properties.

The metric system of weights and measures has been adopted because of its advantages both to the teacher and the student of Dyeing, and it is now becoming more and more generally known and appreciated. For those who prefer the English system, however, tables of equivalents are given at the end of the volume.

Considerable care has been bestowed upon the arrangement of the subject matter, to prevent, on the one hand, confusion arising in the mind of the reader as to which fibre is being referred to in any given connection, and, on the other, to enable comparisons to be readily made of the treatment to which each fibre—cotton, wool, or silk—is submitted when applying any given colouring matter or mordant.

To my old and valued friend, Prof. L. Liechti, of Vienna, I tender my best thanks for his friendly criticisms during the progress of the work, and his kind assistance in the revision of the proofs.

My obligations are also due to those Colour-Manufacturers and Engineers whose names are mentioned in the text, and also to the proprietors of the *Textile Manufacturer*, for the loan of a complete set of their well-known journal.

All the principal English and foreign standard works and journals on dyeing have been consulted, and the information has, as far as possible, been brought down to the latest date.

J. J. H.

Yorkshire College, Leeds.
October, 1885.

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CHAPTER I.

COTTON.

1. The Cotton-Plant.—Cotton is the white, downy, fibrous substance which envelopes the seeds of various species of the cotton-plant, *Gossypium*, belonging to the natural order *Malvaceæ*. The seeds, to which the cotton fibres are attached, are enclosed in a 3- to 5-valved capsule, which bursts when ripe; the cotton is then collected and spread out to dry. The seeds are afterwards separated by the mechanical operation termed "ginning," and the raw cotton thus obtained is sent to the spinner. The cotton-plant (Fig. 1) is cultivated with success only in warm climates. There are numerous varieties, of which the following are the principal:—


Fig. 1.—Cotton Plant.

(1) *Gossypium barbadense.*—An herbaceous plant, bearing a yellow flower, and attaining a height of 4–5 metres.

A variety of this species yields the Sea Island cotton, much prized on account of the great strength, length, and lustre of its fibres. It is grown in the North American States of South Carolina, Georgia, and Florida, and on the neighbouring islands of the West Indies.

(2) *Gossypium hirsutum.* — A hairy, herbaceous plant, about 2 metres high, with pale yellow or almost white flowers. It is grown in the States of Alabama, Louisiana, Texas, and Mississippi.

(3) *Gossypium herbaceum.* — A small herbaceous plant, 1 metre high, and bearing yellow flowers. Varieties of this species are grown in India, China, Egypt, and America.

The Madras, Surat, and short-stapled Egyptian cotton, also some American cottons, are obtained from this species.

(4) *Gossypium peruvianum.*—This species, a native of South America, grows to a height of 3–5 metres, and bears a yellow flower. It yields the long-stapled and much esteemed Peruvian and Brazilian cottons.

(5) *Gossypium religiosum.*—This is a low annual shrub, about 1 metre high, and bearing a yellow flower. It is grown in China and India, and yields the so-called Nankin cotton, remarkable for its tawny colour.

(6) *Gossypium arboreum.*—This is a perennial tree, growing to a height of 6–7 metres, and bearing reddish-purple flowers. It is a native of India, and produces a good quality of cotton.

2. **Physical Structure.**—If cotton wool is examined under the microscope, it is seen to consist of minute fibres. Their general appearance is that of spirally-twisted bands, having thickened borders and irregular markings on the surface (Fig. 2). In the better qualities of cotton—*e.g.*, Sea Island—the spiral character is less

prominent. Transverse sections of the fibres show them to be flattened tubes, having comparatively thick walls and a small central opening (Fig. 3).

A single cotton fibre is, indeed, an elongated, tapering, and collapsed plant-cell, the thin end of which is closed, and the other (namely, that by which it was attached to the seed) irregularly torn. Sometimes broad ribbon-like fibres may be noticed, which are remarkably transparent, and possess irregular folds. Their transverse section exhibits no central opening at all (Fig. 4). They are, indeed, unripe fibres, in which no separation of the thin cell walls has yet taken place. They refuse to be dyed like ordinary ripe fibres, and appear occasionally as white specks in indigo- and madder-dyed calicoes; hence the name *dead cotton* has been given to them. In half-ripe cotton fibres the cell walls are still so closely pressed together that the ultimate central canal is indicated in a transverse section only by a fine line. When steeped in water, however, such fibres gradually swell up and form hollow tubes. Cotton fibres vary in length from 2·5 to 6 centimetres, and in breadth from 0·017 to 0·05 millimetres.

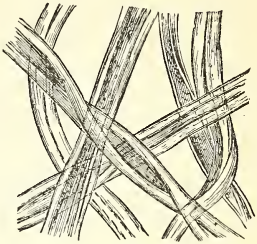


Fig. 2.—Appearance of Cotton under the Microscope.

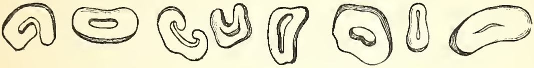


Fig. 3.—Transverse Sections of Cotton Fibre.

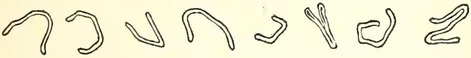


Fig. 4.—Transverse Sections of Unripe Cotton Fibre.

The spiral character of the fibre makes it possible to spin exceedingly fine yarn, and also accounts for the elastic character of calico as compared with linen, the fibres of which are stiff and straight. The microscopic appearance of cotton serves to distinguish it from other vegetable and animal fibres.

3. **Chemical Composition.**—The substance of the cotton fibre is called *Cellulose.* This is almost universal in vegetable cells, forming the so-called ligneous matter or woody fibre of plants, but whereas in woody fibre the cellulose is encrusted with a large proportion of foreign matter—such as dried-up sap, resin, &c.,—in the cotton fibre it is in a tolerably pure condition. The impurities present amount to about 5 per cent., this being the loss sustained by raw cotton when submitted to the process of bleaching, the main object, indeed, of which is the total removal of these impurities. The principal bleaching operation consists in boiling the cotton with a solution of sodium carbonate or hydrate. From the dark brown solution thus obtained, acids throw down a voluminous light brown precipitate, which, when washed and dried, amounts only to about 0·5 per cent. of the weight of cotton employed. This precipitate is found to consist of the following organic substances:—Pectic acid, brown colouring matter, cotton wax, fatty acids (margaric acid), and albuminous matter. Pectic acid exists in the largest proportion, and it is not improbable that the 4·5 per cent. loss by bleaching still unaccounted for, represents certain pectic matters, modified and rendered soluble by the action of alkalis, but not precipitated by acids.

In addition to the above-mentioned impurities of the cell wall, the raw cotton fibre seems to be covered with an exceedingly delicate membrane, or cuticle, which is not cellulose. If cotton, when under microscopical observation, be moistened with an ammoniacal solution of cupric hydrate, the fibre swells up under its influence, whereas the cuticle is unaffected and shows itself as band-like strictures or rings of various breadths. If a drop of sulphuric acid be then added, the cellulose separates out as a gelatinous mass, which, on adding a drop of iodine solution, becomes coloured blue, whereas the cuticle is coloured yellow. By moving the cover-glass aside a little, the cuticle rings are seen to be in the form of tubes, possessing apparently a spiral structure. Some observers state that during the bleaching process this cuticle is removed, while others say this is not the case. The average moisture in raw cotton is about 8 per cent., so that, reckoning the 5 per cent. impurities already alluded to, one may consider that raw cotton contains 87 per cent. of pure dry cellulose.

When submitted to chemical analysis, cellulose is found to be composed of carbon, hydrogen, and oxygen, the formula assigned to it being $C_6H_{10}O_5$. It is closely allied in composition to starch, dextrin, and glucose, and is classed along with them as a carbo-hydrate. It is colourless, possesses neither taste nor smell, and has a density of about 1·5. If heated above 130° C. it becomes brown, and begins to decompose. In contact with air it burns without emitting any very strong odour, a fact which may sometimes serve to distinguish it from wool and silk. It is quite insoluble in the ordinary solvents, water, alcohol, ether, &c., but, as already indicated, it dissolves in an ammoniacal solution of cupric hydrate; from this it is precipitated by acids as a gelatinous mass, which, when washed with alcohol, forms an amorphous white powder.

Action of various Agencies on Cotton.

4. **Action of Mildew.**—Owing to its comparative freedom from impurity, cotton may be stored for a long period without undergoing any change, more especially if it is bleached and kept dry. When, however, it is contaminated with added foreign organic matter, such as starch, gum, &c. (*e.g.*, in "finished" calicoes), and then exposed to a moist, warm atmosphere, it is very liable

gradually to become tender or rotten. This is owing to the growth of vegetable organisms of a very low order, generally called "mildew." These fungi feed upon the starchy matters present, inducing their decomposition, and after some little time the cotton fibres themselves are attacked. The simultaneous production of crenic, humic, ulmic, and other organic acids may possibly assist somewhat in the tendering process.

5. Action of Frost.—It has been supposed by some that wet calico is tendered when it is frozen. Although the evidence on this point is conflicting, it is quite conceivable that the crystallisation might act injuriously in a mechanical way, and that the atmospheric ozone might also exercise some slight destructive influence. The popular notion probably arises from the fact that in their rigid state the cotton fibres are readily broken. A similar friable condition is obtained by excessive stiffening with starch or gum.

6. Action of Acids.—Cold dilute mineral acids have little or no action, but if allowed to dry upon the cotton they gradually become sufficiently concentrated to corrode and tender the fibre. The physical structure of the fibre is not affected, but the chemical composition of the disintegrated fibre seems to be somewhat altered: it contains more oxygen and hydrogen. The same corrosive action soon takes place if cotton impregnated with such acids is heated. The process of "extracting" or "carbonising" woollen rags containing cotton (*i.e.*, destroying and removing the cotton), by means of sulphuric or hydrochloric acid, is founded on this fact.

The action of strong acids varies considerably according to the nature, concentration, and temperature of the acid, as well as the duration of its contact with the fibre.

Very concentrated *sulphuric acid* causes cotton to swell up, and form a gelatinous mass, from which, on the addition of water, a starch-like substance termed Amyloid may be precipitated. A solution of iodine colours this amyloid blue. Vegetable parchment is paper (cellulose) superficially changed into amyloid by a short steeping in strong sulphuric acid 140° Tw. (Sp. Gr. 1·7), then washing and drying. An increased affinity for basic coal-tar colouring matters is said to be imparted to cotton by this treatment, even when the acid is diluted to 84° Tw. (Sp. Gr. 1·42), although its physical aspect then remains unchanged. Cotton completely disorganised by acid, and obtained as a fine powder, seems to contain one molecule of water more than ordinary cellulose, and the substance thus produced has been termed Hydro-cellulose.

If the concentrated sulphuric acid is allowed to act for a longer time, the cotton dissolves with the formation of a different substance of a gummy nature, called Dextrin ($C_6H_{10}O_5$); when the solution is diluted with water and boiled for some time, this dextrin is further changed into Glucose ($C_6H_{12}O_6$).

If cotton be heated with strong *nitric acid* it is entirely decomposed, producing oxalic acid and an oxidised cellulose soluble in alkalis. By the action of cold concentrated nitric acid, or, better still, a mixture of strong nitric and sulphuric acids, cellulose is changed into so-called Nitro-cellulose. The physical structure of the cotton remains the same, although increased in weight by more than 5 per cent., but its chemical composition and properties are very much altered, certain elements of the nitric acid having replaced a greater or less proportion of the hydrogen of the cellulose. The most highly nitrated compound is Pyroxylin, or Gun-cotton ($C_{12}H_{14}(NO_2)_6O_{10}$), produced by the short action of a very concentrated mixture of acids; it is very explosive, and insoluble in alcohol and ether. The less nitrated product, obtained by the longer action of more dilute acids, forms the so-called Soluble Pyroxylin. Its solution in a mixture of ether and alcohol constitutes Collodion, which on evaporation leaves the pyroxylin as a thin, transparent, horny film, insoluble in water. It was long ago noticed by Kuhlmann that gun-cotton had an increased affinity for colouring matters, but no practical use has been made of the fact.

Strong *hydrochloric* and *phosphoric acids* behave towards cotton like sulphuric acid, but their action is less energetic. Although the ultimate product of the action of hydrochloric acid or cotton is the same as that given by sulphuric acid, there is never any intermediate formation of amyloid.

Solutions of *tartaric, citric, and oxalic acids* have no destructive action on cotton if it is simply steeped in the liquid; but if cotton saturated with a solution containing 2 per cent. of any of the above acids is dried and heated for an hour to 100° C., it becomes slightly tendered. With 4 per cent. solutions the destructive action is very decided at 100° C., and perceptible even at 80° C. Oxalic acid has the most injurious effect in this respect. If the acid solutions are thickened with gum or starch, and if steaming be substituted for a dry heat, the corrosive action in each case is less marked, so that in the ordinary practice of the calico-printer, who frequently uses steam-colours containing 4 per cent. or more of the above acids, there is little to fear. Still, it is well to bear in mind that even organic acids cannot under all circumstances be applied to cotton with impunity.

Acetic acid may be considered as having no perceptible action on cotton.

7. Action of Alkalis.—Weak solutions of *caustic potash* or *soda*, when used cold, have, under ordinary circumstances, no action on cotton, although long-continued and intermittent steeping and exposure to air tender the fibre. Cotton may even be boiled for several hours with weak caustic alkalis, if care be taken that it remains steeped below the surface of the solution during the whole operation, but otherwise it is very liable to become rotten, especially if the exposed portions are at the same time under the influence of steam. Such exposure is to be guarded against during certain of the operations in bleaching cotton fabrics. The tendering action is probably due to oxidation. It is worthy of note that the disorganised fibre (oxy-cellulose) possesses an increased attraction for basic coal-tar colouring matters.

In the case of raw cotton, the action of boiling with weak caustic alkalis is simply to remove those natural impurities already referred to, which cause it to be water-repellent, and therefore difficult to wet by mere steeping in cold water.

The action of *strong* solutions of caustic potash or soda is very remarkable. If a piece of calico is steeped for a few minutes in a solution of caustic soda, marking about 50° Tw. (Sp. Gr. 1·25), it assumes quite a gelatinous and translucent appearance; when taken out and washed free from alkali, it is found to have shrunk considerably, and become much closer in texture. If a single fibre of the calico thus treated be examined under the microscope, it is seen to have lost all its original characteristic appearance; it has no superficial markings, and is no longer flat and spirally twisted, but seems now to be thick, straight, and transparent. A transverse section shows it to be cylindrical, while the cell walls have considerably thickened, and the central opening is diminished to a mere point (Fig. 5). Many years ago a Lancashire calico-printer, John Mercer, discovered that calico treated in the above manner was not only stronger than before, but had also acquired an increased attraction for colouring matters. Hoping to apply the process with advantage preparatory to dyeing, he patented it. Cotton thus treated is said to be Mercerised. When dyed in the indigo-vat, mercerised calico requires only one dip to produce as deep a shade of blue as can be obtained on ordinary calico only after five or six dips. Again, if a piece of ordinary and a piece of mercerised calico be dyed

Fig. 5.—Transverse Sections of Cotton Fibre after Treatment with Caustic Soda.

alizarin red, making all other conditions (*e.g.*, time, temperature, quantity of Alizarin, &c.) the same in both cases, the mercerised cloth will be found to have a much fuller and richer colour than the other. Similar differences in depth of shade are noticed with other colours. The process, however, has never been adopted in general practice, since the excessive contraction which the cloth undergoes, amounting as it does to one-fifteenth in length and in breadth, and the fact that in most cases the same result can be obtained in other ways, did not seem to warrant the expense.

Caustic ammonia in aqueous solution, whether strong or weak, has under all circumstances no action on cotton. Dry cotton is said to absorb one hundred and fifteen times its bulk of ammonia gas. Solutions of the *carbonates of potash, soda* or *ammonia, silicate of soda, borax,* and *soap,* have practically no action on cotton. There is a case on record, however, in which calico impregnated with silicate of soda, and shipped from England to South Africa, was found, after having been packed in bales for two years, to have become tender. Examination showed that the silicate of soda had decomposed with formation of silicic acid and carbonate of soda, and it was concluded that the tendering was due partly to the long-continued action of the carbonate of soda on the cotton, and partly to disruption of the fibres by the expansive force of the crystallisation of the carbonate of soda formed within them. The explanation is not altogether satisfactory, since it was found impossible to produce the same effects artificially. Probably it was a case of oxidation of the fibre. Whatever may have been the real cause, it is well to bear in mind that under exceptional conditions like those mentioned, even apparently harmless salts may tender the cotton fibre.

8. **Action of Lime.**—Milk of lime, even at a boiling heat, has little or no action upon cotton so long as the latter is steeped below the surface of the liquid, but if it is at the same time exposed to the action of air or

steam, it becomes much tendered by oxidation of the fibre. Such exposure must be avoided in cotton-bleaching.

9. **Action of Chlorine and Hypochlorites on Cotton.**—Cotton is quickly tendered if exposed to moist *chlorine gas*, especially in strong sunlight. The action may be due partly to the direct action of chlorine upon the fibre, one portion combining with and another replacing some of its hydrogen, partly to the destructive action of the hydrochloric acid thus produced, and partly to oxidation. Solutions of *hypochlorites* (bleaching-powder, &c.) tender cotton more or less readily, according to the strength and temperature of the solutions and the duration of their action. Even a very weak solution of bleaching-powder will tender cotton if the latter be boiled with it; but when used cold, even if it be at the same time exposed to the air, the destructive action is inappreciable, and confined merely to bleaching the natural colouring matter of the cotton. If a piece of calico is moistened with a solution of bleaching-powder at 5° Tw. (Sp. Gr. 1·025), then exposed to the air for about an hour, and washed, it will be found to have acquired an attraction for basic coal-tar colouring matters similar to that possessed by the animal fibres. Cotton thus treated also decomposes directly the normal salts of aluminium, iron, &c., attracting metallic oxide. Experiment has shown that this remarkable change is due to the action of the hypochlorous acid liberated by the carbonic acid of the air. The cotton thereby becomes chemically changed to what has been called by Witz, its discoverer, Oxy-cellulose.

10. **Action of Metallic Salts.**—Under ordinary circumstances, solutions of neutral salts have no action on cotton; even those of acid salts have no appreciable effect if the cotton be merely steeped in them while cold; but if boiled with them the effect is similar to that of the free acids, though slightly less marked. If cotton is impregnated with solutions of the salts of the earths and heavy metals, then dried, and heated or steamed, the salts

are readily decomposed; a basic salt is precipitated on the fibre, and the liberated acid affects the fibre according to the nature and strength of the salt solution employed.

The use of aluminium chloride, which was at one time recommended for the purpose of destroying the cotton in rags containing cotton and wool ("extracting"), also the application of the "topical" or "steam colours," and the "mordanting" process employed by the calico-printer, are all based upon the above facts.

11. Action of Colouring Matters.—With few exceptions, colouring matters are not directly attracted from their solutions by the cotton fibre, hence it is not readily dyed, and special means of preparing it to receive the dyes have to be adopted in most cases (mordanting). The reason of this inert character of cotton is not yet satisfactorily explained; probably both its chemical and physical structure have an influence in the matter.

CHAPTER II.

FLAX, JUTE, AND CHINA GRASS.

12. Flax-plant.—The term "flax" is employed to designate the flax or linen fibre and also the plant from which it is obtained. Linen fibre consists of the bast cells of certain species of the genus *Linum*, more particularly *Linum usitatissimum* (Fig. 6), a plant belonging to the natural order *Linaceæ*, and cultivated in nearly all parts of Europe.

It is an herbaceous plant, having a thin, spindle-shaped root, a stem usually branched at the top, smooth lanceolate leaves, and bright blue flowers.

The time of sowing varies in different countries from

February to April, consequently the time of harvest also varies, and may be from June to September.

Fig. 6.—Flax plant, A; flower, B; fruit, C.

If the object of the farmer is to obtain good fibre, and not seed for re-sowing, the plant is gathered before it is fully matured — namely, when the lower portion of the stem (about two-thirds of the whole) has become yellow, and the seed capsules are just changing from green to brown. At this stage the plants are carefully pulled up. If the plants are left in the ground till the whole stem is yellow—*i.e.*, till the plant is fully ripe—the fibre afterwards obtained will be more stiff and coarse.

The freshly-pulled flax is at once submitted to the process of "rippling," which has for its object the removal of the seed capsules. This operation is performed by hand, by drawing successive bundles of flax-straw through the upright prongs of large, fixed iron combs, or "ripples." If the pulled flax has been dried and stored, the removal of the seeds is usually effected by the seeding-machine, which consists essentially of a pair of iron rollers, between which the flax-straw is passed.

13. Retting. — The most important operation in separating the fibre is that of "retting," the object of which is to decompose and render soluble by means of fermentation, as well as to remove, certain adhesive substances which bind the bast fibres not only to each other, but also to the central woody portion of the stem, technically termed the "shive," "shore," or "boon."

The various modes of retting may be classified as follows:—

(1) Cold-water retting. This may be carried out either with running or with stagnant water.

(2) Dew retting.

(3) Warm-water retting.

Cold-water Retting.—The best system of retting in *running water* is said to be practised in the neighbourhood of Courtrai, in Belgium, where the water of the sluggish river Lys is available. The bundles of flax straw are packed vertically in large wooden crates lined with straw. Straw and boards are afterwards placed on the top, and the crate thus charged is anchored in the stream and weighted with stones, so that it is submerged a few inches below the surface. In a few days fermentation begins, and as it proceeds additional weight must be added from time to time, in order to prevent the rising of the crates through the evolution of gas. As a rule, after steeping for a short period, the flax is removed from the crates, and set up in hollow sheaves to dry; it is then repacked in the crates, and again steeped until the retting is complete. According to the temperature, quality of flax, &c., the duration of the steeping may be from ten to twenty days. The end of the process must be accurately determined by occasionally examining the appearance of the stems, and applying certain tests. The flax bundles should feel soft, and the stems should be covered with a greenish slime, easily removed by passing them between the finger and thumb; when bent over the forefinger the central woody portion should spring up readily from the fibrous sheath. If a portion of the fibre is separated from the stem and suddenly stretched, it should draw asunder with a soft, not a sharp, sound.

When the retting is complete, the flax is carefully removed from the crates and set up in sheaves to dry.

Retting in *stagnant water* is the method usually adopted in Ireland and Russia. The flax in this case is steeped in ponds, situated near a river if possible, and provided with suitable arrangements for admitting and running off the water.

This mode of retting is more expeditious than when running water is employed, because the organic matters retained in the water very materially assist the fermentation; there is, however, always a danger of "over-retting," that is, the fermentation may become too energetic, in which case the fibre itself is attacked and more or less weakened. This danger is minimised by occasionally changing the water during the steeping process. The quality of the water employed in retting is of considerable importance; pure soft water is the best, calcareous water being altogether unsuitable.

The waste flax water, being strongly impregnated with decomposing organic matter, poisons the streams into which it may run, and destroys the fish; but it possesses considerable value as a liquid manure.

After retting in stagnant water, the flax is drained, then thinly spread on a field; it is left there for a week or more, and occasionally turned over. This process is termed "spreading," or "grassing." Its object is not merely to dry the flax, but to allow the joint action of dew, rain, air, and sunlight to complete finally the destruction and removal of the adhesive substances already alluded to. After a few days' exposure the stems begin to "bow," the fibrous sheath separates more or less from the woody centre, and the latter becomes friable.

Dew retting simply consists in spreading the flax on the field and exposing it to the action of the weather for six or eight weeks, without any previous steeping. Damp weather is the most suitable for this method, since all fermentation ceases if the flax becomes dry. Dew retting is practised largely in Russia and in some parts of Germany.

Warm-water retting was a system recommended in 1847 by R. B. Schenck. It consists in steeping the closely packed flax bundles in covered wooden vats, filled with water heated to 25°—35° C. By this means the fermentation is much accelerated, and the operation is completed in two or three days; the process seems, however, to have met with only limited success.

Of *chemical retting* processes, that recommended by R. Baur may be mentioned. It consists in first squeezing the fresh or dried flax straw between rollers, and then steeping it in water till the latter ceases to be coloured yellow. It is next drained and steeped for one or two days in dilute hydrochloric acid (3 kilos. concentrated HCl per 100 kilos. flax), until the bast fibres can be readily separated. The acid liquid is then run off, and the flax is well washed with slightly alkaline water, or such as contains a little chalk. A further treatment with dilute bleaching powder solution to dissolve away still adhering woody matter, and a final washing, complete the process. A well-retted flax is said to be thus obtained in the course of a few days only.

14. Chemistry of Retting.—Experiments by Kolb indicate that the adhesive matter which cements the flax fibres together is essentially a substance called *pectose*. During the retting process the fermentation decomposes this insoluble pectose, and transforms it into soluble *pectine*, and insoluble *pectic acid*. The former is washed away, the latter remains attached to the fibre.

15. Breaking.—The next operation is to remove the woody centre from the retted and dried flax, after which the fibres must be separated from each other. It is rather beyond the province of this manual to give more than a general account of the nature of the various mechanical operations for effecting this. They comprise "breaking," "scutching," and "hackling."

The first operation aims at breaking up the brittle woody centre of the flax into small pieces, by threshing it with an indented wooden mallet, or by crimping it with a many-bladed "braque." The operation is now extensively done by machinery, the flax being passed through a series of fluted rollers.

16. **Scutching.**—In this process handfuls of the flax are beaten with a broad wooden scutching-blade; the particles of woody matter adhering to the fibres are thus detached; and the bast is partially separated into its constituent fibres. Scutching is also performed by machinery. The waste fibre obtained is called "scutching tow," or "codilla."

17. **Hackling.**—The subsequent *Hackling*, or *Heckling*, has for its object a still further separation of the fibres into their finest filaments, by combing. When done by hand, a bundle of flax is drawn, first one end and then the other, through a succession of fixed upright iron combs or "hackles" of different degrees of fineness, beginning with the coarsest. When machinery is used, the flax is held against hackles fixed on moving belts or bars or on the circumference of revolving cylinders. The product of the operation is twofold, namely, "line" and "tow"; the former consists of the long and more valuable fibres, the latter of those which are short and more or less tangled.

18. **Flax-Line.**—The appearance of flax-line is that of long, fine, soft, lustrous fibres, varying in colour from the yellowish-buff of the Belgian product to the dark greenish-grey of Russian flax. This difference in colour is chiefly owing to the system of retting adopted.

Flax retted in running water has a more or less pale yellowish-buff colour, while that retted in stagnant water possesses a greyish colour, probably because of the presence of the decomposing organic matter in the water.

19. **Physical Structure and Properties.**—Examined under the microscope, a single flax fibre appears (Fig. 7)

as a long, straight, transparent tube, often striated longitudinally; it possesses thick walls, and an excessively minute central canal.

At irregular intervals it is slightly distended, and at these points faint transverse markings may be detected. When examined with high powers, they seem to consist of a succession of very minute fissures, and, according to Vetillart, are simply breaks, or wrinkles, produced by a bending of the fibre, and not cell divisions, or nodes, as frequently stated. Fibres which have been vigorously rubbed between the fingers, or have been subjected to the lengthened disintegrating action of alkalis, exhibit well-marked longitudinal fissures, and the broken end of a well-worn fibre presents the aspect of a bundle of fibrils. These appearances evidently indicate that the cell wall of the linen fibre possesses a fibrous structure.

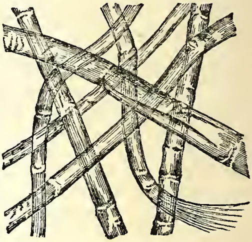


Fig. 7.—Flax Fibre under the Microscope.

The average length of a single fibre is 25–30 millimetres, and the average breadth 0·020–0·025 millimetres.

In transverse section, the linen fibre shows a more or less rounded polygonal contour.

The chief physical characteristics of the linen fibre, when freed from all encrusting material, are its snowy whiteness, silky lustre, and great tenacity. This last feature is no doubt owing to its fibrous texture as well as to the thickness of the cell walls. Its straight, even, prismatic, and transparent character accounts largely for the lustre.

Linen is hygrometric to about the same degree as cotton, and contains, when air-dry, about 3 per cent. of moisture. It is, however, a much better conductor of heat, and therefore feels colder than cotton. It is also less pliant and less elastic.

20. Chemical Composition.—Treated with sulphuric acid and iodine solution, the thick cell wall is coloured blue, while the secondary deposits, immediately enclosing the central canal, acquire a yellow colour. The linen fibre consists therefore essentially of cellulose, but in its raw unbleached state it is mixed with about 15–30 per cent. of foreign substances, chief among which is pectic acid. Fatty matter, to the extent of about 5 per cent., colouring matter, and other substances not investigated, are also present.

Action of various Agencies on Flax.

20*—Being cellulose, the action of various chemical agents on pure linen fibre is much the same as on cotton, but generally speaking, linen is more susceptible to disintegration, especially under the influence of caustic alkalis, calcium hydrate, and strong oxidising agents, *e.g.*, chlorine, hypochlorites, &c.

As to the action of these agents on the encrusting materials of retted flax, boiling solutions of caustic and carbonated alkalis saponify and remove the fatty matter, and also decompose the pectic acid and any pectose which may have escaped the action of the retting process. Under their influence the insoluble pectic acid is changed into metapectic acid, which at once unites with the alkali to form a soluble compound. By successive boiling with alkali the fibre entirely loses its brownish colour, and retains only a pale grey shade, readily bleached by hypochlorites. The system of bleaching linen is based on these reactions.

Water-retted flax (whether retted in running or stagnant water, it matters not) is capable of being well bleached. Under the influence of boiling alkalis it always assumes a lighter colour, and when submitted to the reducing action of stannous chloride it acquires a yellowish tint. Dew-retted flax, on the contrary, bleaches with much difficulty. When boiled with alkalis it becomes darker, and stannous chloride has little or no effect on it.

These reactions may serve to discover by which process of retting the fibre has been obtained.

The linen fibre is even less readily dyed than cotton, a fact which, although well known to dyers, has not yet been satisfactorily explained. Its physical structure and the possible presence of pectic matters no doubt exercise some restraining influence.

21. **Jute** consists of the bast fibres of various species of *Corchorus* (*e.g.*, *C. olitorius*, *C. capsularis*, &c.), belonging to the family of the *Tiliaceæ*, and is mainly cultivated in Bengal. The fibre is separated from the plant by processes similar to those employed in obtaining the flax fibre, namely, retting, beating, washing, drying, &c. The raw fibre, as exported, consists of the upper five-sixths of the isolated bast, and occurs in lengths of about seven feet. Under the microscope, it is seen to consist of bundles of stiff, lustrous, cylindrical fibrils, having irregularly-thickened walls, and a comparatively large central opening. The colour of the fibre varies from brown to silver-grey. It is distinguished from flax by being coloured yellow, under the influence of sulphuric acid and iodine solution.

According to Cross and Bevan, the substance of the jute fibre is not cellulose, but a peculiar derivative of it, to which the name *bastose* has been given. Under the influence of chlorine, a chlorinated compound is produced, which, when submitted to the action of sodium sulphite, developes a brilliant magenta colour. This colour reaction is also exhibited by tannin-mordanted cotton, with which jute shows great similarity; this is further exemplified by the fact that jute can be readily dyed in a direct manner with basic coal-tar colouring matters.

Jute may indeed be considered as consisting of cellulose, a portion of which has become more or less modified throughout its mass into a tannin-like substance. Alkalis actually resolve jute into insoluble cellulose and soluble bodies allied to the tannin matters. Further, when large masses of jute are allowed to lie in a damp state, the substance of the fibre is decomposed into two groups of bodies, namely, acids of the pectic class, and tannin-like substances.

Acids, notably mineral acids, even at low temperatures, readily disintegrate jute, resolving it into soluble substances. This destructive action of acids must be specially borne in mind by the dyer and bleacher of jute.

Strong solutions of hypochlorites produce the chlorinated compound above alluded to, and there is then always a danger of the fibre being disintegrated by subsequent manufacturing operations, *e.g.*, steaming. Weak solutions bleach the fibre to a pale cream colour, at the same time oxidising it, and thus forming compounds which precipitate soluble calcium salts. In bleaching jute, therefore, weak sodium hypochlorite should be used in preference to ordinary bleaching-powder (calcium hypochlorite), since the presence of soda prevents the formation both of the chlorinated fibre and of insoluble calcium compounds. By thoroughly impregnating the bleached fibre with sodium bisulphite, and drying at 80°—100° C., the colour is still further improved through the action of the disengaged sulphurous acid; the neutral sodium sulphite remaining in the fibre prevents its oxidation and disintegration under the influence of ordinary atmospheric conditions, and even steaming. Jute is readily bleached by the successive action of permanganates and sulphurous acid. The loss of weight experienced by jute in bleaching may vary from 2 to 8 per cent., according to the method employed.

22. **China Grass.**—This fibre, also called Rheea, Ramie, &c., consists of the bast cells of *Boehmeria nivea* (*Urtica nivea*), a perennial shrub belonging to the nettle family, *Urticaceæ.* The plant grows abundantly in China, Japan, and the Eastern Archipelago generally. No perfectly satisfactory method of obtaining the fibre with little loss has yet been devised; the native methods of splitting and scraping the plant stems, steeping in

water, &c., are tedious and expensive, while the ordinary retting process is not thoroughly effective, because of the succulent nature of the stem, and the large amount and acridity of the gummy matters, which rapidly coagulate and become insoluble on exposure to air. The chief characteristics of the fibre are its excessive strength and durability, fineness, silky lustre, and pure white colour. Sulphuric acid and iodine solution colour it blue, hence it seems to consist essentially of cellulose. Under the microscope, the fibres appear stiff and straight, the cell walls exhibiting a fibrous texture, and varying in thickness in different parts of the fibre.

CHAPTER III.

WOOL.

23. Varieties of Wool.—By the term "wool" we describe the hairy covering of several species of mammalia, more especially that of the sheep. It differs from hair, of which it may be regarded as merely a variety, by being, as a rule, more flexible, elastic, and curly, and because it possesses certain details of surface-structure which enable it to be more readily matted together.

Many mammalia have both wool and hair, and it is probable that this has also been the case with the sheep in its original wild state, but under the influence of domestication the rank hairy fibres have largely disappeared, while the soft under-wool round their roots has been singularly developed. At so early a date was the sheep domesticated—as remote, indeed, as the prehistoric period of the Cave Dwellers,—that it has been found impossible to determine with certainty its true origin. By some the parent stock is considered to be the *Ovis ammon* of the mountains of Central Asia, where the tribes have always been pastoral in their habits and occupations.

The climate, breed, food, and rearing of the sheep, all influence the quality of the wool. When they are fed upon herbage grown in chalky districts, for example, the wool is apt to be coarse, whereas it becomes fine and silky on those reared upon a rich loamy soil.

Sheep's wool varies from the long, straight, coarse hair of certain varieties of the English sheep (Leicester, Lincolnshire, &c.), to the comparatively short, wavy, fine, soft wool of the Spanish Electoral sheep.

Down to the end of the last century the Spanish Merino sheep yielded the finest and best wool in the world. About that period this variety was imported into nearly every country in Europe, and by dint of careful selection and good breeding, the wool-growers of Saxony and Silesia at length succeeded in producing wool which quite equalled that of the original Spanish race. Merino sheep have since been introduced into Australia, the Cape of Good Hope, New Zealand, &c.; and these so-called Colonial wools, so much used and appreciated at the present time, all bear the Merino character derived from the original Spanish stock.

According to the average length of the fibres comprising the locks of wool, or "staple," two principal classes of wool may be distinguished, namely, the *long-stapled* (18–23 centimetres) and the *short-stapled* wools (2·5–4 centimetres). In the process of manufacture into cloth, the former require to be *combed*, and serve for the production of so-called "worsted" goods, while the latter are *carded*, and used for "woollen" goods. It is well to add that this distinction between worsted and woollen goods refers rather to the operations of combing and carding than to the length of staple of the wool employed, since large quantities of worsted are made from short wool. The essential difference is really owing to a different arrangement of the fibres in the yarn. The diameter of the wool fibre may vary from 0·007 to 0.5 millimetre.

Very marked differences exist even in the wool of a single animal, according to the part of the body from which it is taken, and it is the duty of the *wool-sorter* to distinguish and separate the several qualities in each fleece.

24. **The Physical Structure** of the wool fibre is very characteristic, and enables it to be readily distinguished from other textile fibres. Being a product of the epidermal layer of the skin, it is built up of an immense number of epithelial cells. When carefully examined under the microscope, a wool fibre is seen to consist of at least two parts, sometimes even of three.

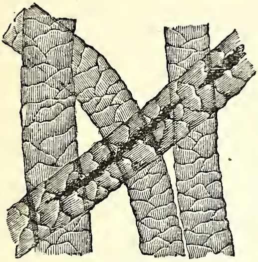


Fig. 8.—Microscopical Appearance of Wool Fibre.

(1) The external cells appear as thin horny plates or scales of irregular shape; they are arranged side by side and overlapping each other, somewhat after the manner of roof-tiles (Fig. 8). The upper edges are more or less free, the lower are apparently imbedded in the interior of the fibre. In merino *wool* the scales appear funnel-shaped, and fit into each other, each one entirely surrounding the fibre. In *hair* they are more deeply imbedded; they also lie flatter, and present but little free margin.

This surface-character plays an important part in causing the "felting" of wool in "milling," &c. During this and similar operations, in which a large number of fibres are brought into close and promiscuous contact, each fibre naturally moves more readily in one direction than in the other, and the opposing scales gradually become interlocked.

(2) The cortical substance of the wool fibre

constituting nearly, and sometimes entirely, the whole internal portion of the fibre, is composed of narrow spindle-shaped cells, which have assumed a more or less horny character. This structure, which gives the inner portion of a wool fibre a fibrous appearance when examined longitudinally under the microscope, is best seen after gently heating the fibre with sulphuric acid. By means of a pair of dissecting needles it is then readily separated into its constituent cells.

In Figure 9, B represents the microscopic appearance of the fibre after treatment with acid, and A shows some of the individual cells.

It is an interesting fact that these disintegrated internal cells possess a greater attraction for colouring matter than the external scales, and the beneficial effect of the acidity of the bath, required in many cases of mordanting and dyeing, may possibly be ascribed to the opening out of the epithelial scales and the exposure of the inner fibrous cells to the action of the liquid of the bath. This seems to explain also why "extracted" or "carbonised" wool dyes deeper shades and more rapidly than ordinary wool.

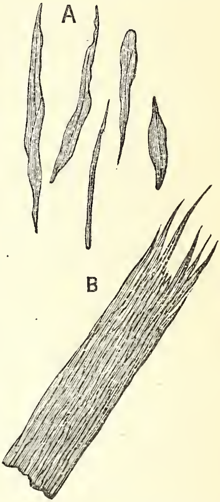


Fig. 9.—Cells of Wool Fibre under the Microscope.

(3) The central, or medullary, portion of the wool fibre, when present, is formed of several layers of rhombic or cubical cells, which appear as the marrow or pith of the fibre, and may traverse its whole length or appear only in parts. By boiling the fibre with alkali, it is often possible to squeeze out this medullary portion. In many classes of wool (merino, &c.) it seems to be entirely absent: indeed, its presence or absence depends

upon a variety of factors, *e.g.*, race, health of individual, part of the body from which the wool is taken, &c.

In colourless wool the medullary portion often appears under the microscope as a dark or dull hazy stripe. This appearance is caused by the air enclosed between the cells, so that by boiling such a fibre with turpentine or glycerine the cells become transparent.

Wool fibres which exhibit the medullary cells are brittle and stiff; altogether they possess more of a hairy character, and are less suitable than other varieties for manufacturing purposes. In the best qualities of wool the medullary cells are invisible.

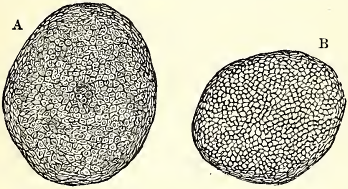


Fig. 10.—Cross Section of typical Wool Fibres.

In a transverse section, a wool fibre appears more or less round or oval.

Figure 10 gives the cross sections, according to F. Bowman, of two typical wool fibres; A shows the medullary, cortical, and external cells; in B the medullary cells are absent.

"Kemps" are certain wool fibres not possessing the normal structure of good wool; under the microscope the epithelial scales are less distinct, or even invisible, and viewed by transmitted light, either the whole substance of the fibre seems more dense and sometimes even opaque, or the medullary portion only is opaque. They are deficient in tenacity, lustre, and felting power, and in their attraction for colouring matters. They may occur even in good qualities of wool, *e.g.*, about the neck and legs of the animals, where the wool gradually merges into hair. In coarse wools they may be found in any part of the fleece.

A merino wool fleece is made up of an immense number of small bundles or strands of wool fibres, which, in the best races of sheep, show a perfectly regular and fine wavy character. The individual fibres are also more or less wavy, but not with the same degree of regularity as the strand of which they form a part. When the fibres adhere to each other, as in the strand, the regular wavy character is very marked.

Besides sheep's wool, the hairy covering of other animals is used in the woollen industry.

25. Foreign Wools.—*Alpaca*, *Vicuna*, and *Llama* wool are obtained from different species of the genus Auchenia (*A. alpaca*, *A. vicugnia*, *A. llama*), which inhabit the mountains of Peru and Chile.

Mohair is obtained from the Angora goat (*Capra hircus angorensis*) of Asia Minor.

Cashmere consists of the soft under-wool of the Cashmere goat (*Capra hircus laniger*) of Tibet.

The soft under-wool of the camel, which it sheds each spring, is also used. Of all these, the alpaca and mohair are most largely employed.

Certain of these foreign wools, more especially Van Mohair, also Alpaca, Camel's hair, Cashmere, and Persian wool, are apt to be dangerous to the health of the wool-sorter. They seem to contain the microscopic organism known as *Bacillus anthracis*, the same which excites splenic fever in cattle and horses. When taken into the bronchial tubes of man, it induces a kind of blood-poisoning known as "wool-sorter's disease." The wool-sorting rooms ought, therefore, to be well ventilated, and the sorters should wear respirators during their work.

26. Physical Properties—*Hygroscopicity.*—The wool fibre is capable of absorbing a large amount of water without appearing damp, *i.e.*, it is very *hygroscopic.* Exposed to the air in warm, dry weather, it contains 8–12 per cent. moisture; but if kept for some time in a damp atmosphere, it may take up as much as 30–50 per cent. This moisture probably fills up the interstices between the cells of the fibre, which under ordinary circumstances contain air, but it no doubt also permeates the substance of the cells themselves. It is noteworthy that damp wool is not so liable to mildew as the vegetable fibres are.

The amount of moisture in unwashed wool varies with the fatty matter it contains, the less fat the more moisture; while in washed wool it depends upon the arrangement of the cells. The wool which has least tenacity—*i.e.*, that in which the cells are more loosely arranged—possesses the greatest hygroscopicity.

This hygroscopic character of wool renders it very desirable that those trading with it should know exactly its condition in this respect at the time of buying and selling, hence, on the Continent, so-called "Wool-conditioning" establishments have been instituted in various centres of the woollen industry—*e.g.*, Roubaix, Rheims, Paris—where the exact amount of moisture in any lot of wool may be officially determined. These establishments are arranged on the same principles as those for silk-conditioning p. 61). As wool is more sensitive to heat than silk, the drying of it is effected between 105°–110° C. The legal amount of moisture allowed on the Continent is 18·25 per cent.

If wool fibre is steeped in warm water, it softens and swells up very considerably, and, like all horny substances, becomes *plastic*, retaining any position which may be forced upon it, if, while the mechanical strain is continued, the moisture is more or less evaporated.

This hygroscopic and plastic nature of wool comes into play in the processes of "crabbing" and "steaming" of unions, in the "boiling" and "finishing" ("hot-pressing") of woollen-cloth, and in the "stretching" of yarn.

Elasticity.—Closely connected with the hygroscopic nature of wool is its *elasticity*, which it possesses in a high degree, not merely because of the wavy character of the fibre, but also on account of its substance and structure. One important manifestation of its elasticity is shown if a dry wool-fibre is excessively stretched; when the ends are released, or rupture takes place, not only does the fibre or do the separated parts rebound to the original position, but an additional shrinking and curling up of the ends are exhibited.

If a single wool fibre is softened by heat and moisture, then stretched and dried in this condition, it is found to have lost this curling property, but it reappears whenever the stretched fibre is again softened, and allowed to dry in an unfettered condition.

In conjunction with pressure, friction, and temperature, many of the above-mentioned physical features—*e.g.*, the scaly surface of the fibre, its waviness, and its hygroscopic, elastic, and plastic nature—play a most important part in the processes of "felting" and "milling" woollen cloth.

The *lustre* of wool varies very considerably. Straight, smooth, stiff wool has more lustre than the curly merino wool. The differences exhibited depend partly upon the internal structure, but chiefly upon the varying arrangement and transparency of the scales on the surface of the fibre; the flatter these are and the more they lie in one plane, the greater will be the lustre. Such wools as possess a silky lustre in a high degree—*e.g.*, Lincoln and Leicester wools, &c.—are classed as *lustre wools*, as distinguished from *non-lustre* wools—*e.g.*, Merino, Colonial, &c.

Wool with a glassy lustre, *e.g.*, bristles, &c., is harder and more horny than non-lustre wool; the surface is smoother, the scales are less distinct, and wools of this kind do not dye so readily.

The best kind of wool is colourless, but lower qualities are often yellowish, and sometimes variously coloured—*e.g.*, black, brown, red, &c. This coloration is caused by the presence of an organic pigment in the cortical portion of the fibre, either as a granular pigment situated between the cells, or as a colouring matter diffused throughout the cell substance. Generally, both forms are present, but in brown and black wool the granular pigment predominates, while in red and yellow wools the diffused colouring matter is more prominent. These natural pigments are not so fast to light as is generally supposed, a fact which is already revealed by the bleached appearance of the exposed portions of the fleece.

The worth of any quality of wool is determined by carefully observing a number of its physical properties—*e.g.*, softness, fineness, length of staple, waviness, lustre, strength, elasticity, flexibility, colour, and the facility with which it can be dyed. *Fleece wool*, as shorn from the living animal, is superior in quality to "*dead wool*," *i.e.*, wool which has been removed from the skin after death, if lime has been used in the process, but if it be removed from the skins by cutting, the wool is practically equivalent to "fleece wool;" indeed, it is said to felt better than the latter. Individual dead fibres occur occasionally in fleece wool; they have been forced out by the roots previous to the time of shearing, and constitute the so-called "overgrown" wool. This class of wool is comparatively harsh and weak, and is said not to dye so readily as other kinds. This is the case also with the wool of an animal which has died of some distemper.

27. **Chemical Composition.**—With regard to the chemical composition of wool, a distinction must be made between the *fibre proper* and the *foreign matters* encrusting it. The latter, while consisting partly of mechanically adhering impurities derived from without, are mainly secreted by the animal, and constitute the so-called *Yolk* (Fr. *Suint*).

Wool fibre which has been entirely cleansed and freed from these foreign matters possesses a chemical composition very similar to that of horn and feathers, and consists of what is termed *Keratin* (horn-substance). Its elementary composition varies somewhat in different qualities of wool, but the following analysis of German wool may be taken as representative :—

Carbon	49·25	per cent.
Hydrogen	7·57	„
Oxygen	23·66	„
Nitrogen	15·86	„
Sulphur	3·66	„
	100·00	

The question as to whether the sulphur is an essential constituent or not has been much discussed. It is removed to a greater or less degree by most solvents, hence it is difficult to obtain constant analytical results. Its amount has been found to vary in different wools from 0·8 to 3·8 per cent. Its constant occurrence, and that in comparatively large proportion, precludes the idea that it is merely an accidental constituent, and it has hitherto been found impossible to deprive wool *entirely* of its sulphur, without, at the same time, modifying somewhat its structure and in large measure destroying its tenacity.

This presence of sulphur in wool is attended with some practical disadvantages. The wool is apt to contract dark-coloured stains under certain conditions, and on that account its contact with such metallic surfaces as those of lead, copper, and tin should be avoided during processes of scouring or dyeing. In mordanting with stannous chloride and cream of tartar, especially if an excess of these ingredients be used, the wool is frequently stained, by reason of the formation of stannous sulphide.

A boiling solution of plumbite of soda at once blackens wool, and may thus serve to distinguish it from silk or cotton.

For practical purposes, much of the sulphur may be removed by steeping the wool in cold weak alkaline solutions—*e.g.*, milk of lime,—then washing it in water, in weak hydrochloric acid, and again with water, repeating the operations several times.

The amount of mineral matter in wool free from yolk varies from 0·08–0·37 per cent. It consists mainly of phosphates and silicates of lime, potash, iron, and magnesia.

Action of various Agencies on Wool.

28. Action of Heat.—If heated to 130° C., wool begins to decompose and give off ammonia; at 140–150° C. vapour containing sulphur is disengaged.

When wool fibre is inserted in flame it burns with some difficulty, and emits a disagreeable odour of burnt feathers. It has the appearance of fusing, a bead of porous carbon being formed at the end of the fibre. Submitted to dry distillation, it gives off products containing much ammonium carbonate, which may be readily detected by its smell or by its colouring red litmus-paper blue. These reactions serve to distinguish wool from all vegetable fibres.

A cold ammoniacal solution of cupric hydrate has no action upon wool, but if it is used *hot* the wool is dissolved.

29. **Action of Acids.**—Dilute solutions of *hydrochloric* and *sulphuric acids* have little influence upon wool, whether applied hot or cold, further than opening out the scales and making the fibre feel somewhat rougher, but if used too concentrated, the fibre is soon disintegrated; in any case their destructive action is by no means so energetic on wool as on cotton. This fact is made use of to separate cotton from wool in the process of "extracting" or "carbonising" rags containing both fibres. The rags are steeped in dilute sulphuric acid, and after removing the excess of liquid, are dried in a stove at about 110° C. The disorganised cotton can then be beaten out as dust, while the wool remains comparatively little injured. Another method is to submit the rags for a few hours to heated hydrochloric acid gas.

The above mineral acids are frequently added to the dye-bath in wool-dyeing.

Nitric acid acts like the acids just mentioned, but it also gives a yellow colour to the wool, owing to the production of so-called xanthoproteïc acid. Because of the comparatively light yellowish colour thus imparted, boiling dilute nitric acid is frequently used as a "stripping" agent for wool, *i.e.*, to destroy the colour in wool already dyed, for the purpose of re-dyeing (job-dyeing, rectifying mistakes, &c.). Care must always be taken not to have the acid too strong (about 3°–4° Tw.—Sp. Gr. 1·02), and not to prolong the process beyond three or four minutes.

Sulphur dioxide (*sulphurous acid gas*) removes the natural yellow tint of ordinary wool, and is the best bleaching agent employed for this fibre. It is important to remember that the gas is very persistently retained by the fibre, and should always be removed from bleached wool previous to dyeing light colours. This is effected by steeping the wool in very dilute solutions of carbonate of soda or bleaching-powder, and washing well. When the first reagent is employed, the acid is merely neutralised, but with the second the sulphurous acid is oxidised to sulphuric acid. Should this precaution be neglected, the wool will not dye properly, or, when dyed, it will be liable to become decolorised again through the reducing action of the sulphur dioxide retained by the fibre.

30. Action of Alkalis.—Alkaline solutions have a very sensible influence on wool, but the effects differ considerably according to the nature of the alkali, the concentration and temperature of the solution, and the duration of contact.

Caustic alkalis (KHO, $NaHO$) act injuriously on wool under all circumstances. Even when they are applied as cold and weak solutions, their destructive action is sufficient to warrant their complete rejection as "scouring" agents.

When they are applied hot, even though but little concentrated, the wool is gradually dissolved, producing a soapy liquid from which it may be precipitated, on the addition of acid, as a white amorphous mass.

This fact of the solubility of wool in hot caustic alkalis is utilised for the purpose of recovering indigo from vat-dyed woollen rags, this colouring matter being insoluble therein.

Solutions of alkaline carbonates and of soap have little or no injurious action on wool, if they are not too concentrated, and the temperature is not higher than 50° C. *Soap* and *carbonate of ammonia* have the least injurious action, while the *carbonates of potash* and *soda* impart to the wool a yellow tint, and leave it with a slightly harsher and less elastic feel.

This marked difference of action between the caustic and carbonated alkalis makes it an all-important matter for every wool-scourer to know the exact nature of the agents he uses: soaps should be free from excess of alkali, "soda ash" should contain no caustic soda, &c.

Calcium hydrate (*lime*) acts injuriously, like the caustic alkalis, but in a less degree. It eliminates the sulphur from the wool, but thereby renders the fibre brittle and impairs its milling properties.

31. **Chlorine and Hypochlorites** act injuriously on wool, and can therefore never be applied to it as bleaching agents. A hot or boiling solution of *chloride of lime* entirely destroys the fibre, with evolution of nitrogen gas; if, however, wool be submitted to a *very slight* action of chlorine or hypochlorous acid, it assumes a yellowish tint, and acquires at the same time an increased affinity for many colouring matters. This effect is possibly due to an oxidation of the fibre, and not merely to a roughening of its surface. Practical use is made of it by the printer of Muslin Delaine (mixed fabrics of cotton and wool) and occasionally by the woollen dyer.

32. **Action of Metallic Salts.**—In common with all fibres of animal origin, wool has the property of readily dissociating certain metallic salts when in contact with their solutions, especially if the latter are heated. When, for example, wool is boiled with solutions of the sulphates, chlorides, or nitrates of aluminium, tin, copper, iron, chromium, &c., a small amount of the oxides or of insoluble basic salts of these metals is deposited upon or attracted by the fibre, and a more acid salt remains in solution. On this fact depends the method of mordanting wool, which differs from that employed with the vegetable fibres, since these do not cause dissociation under like conditions.

Neutral salts of the alkalis (*e.g.*, $NaCl$, Na_2SO_4) exercise no appreciable action on wool.

33. **Action of Colouring Matters.**—Wool has a marked direct attraction for certain colouring matters

(magenta, azo-scarlet, indigo extract, orchil, &c.) if their solutions are presented to it in a proper state of neutrality or acidity, &c., and with these it is dyed with great facility. Being of a porous nature, it is indeed readily permeated by solutions of all colouring matters, especially when heated with the latter.

34. Foreign Matters in Raw Wool-Yolk.—The foreign matter, or *yolk*, enveloping the pure wool fibre possesses a special interest for the dyer, because on its entire removal depends to a very large extent the success with which he may obtain fast, pure, and even colours. To the merchant and manufacturer it is also of great importance, since the amount in different kinds of raw wool varies considerably, and influences its commercial value.

By treating wool first with distilled water, and afterwards with alcohol, Chevreul obtained the following analysis of raw merino wool dried at 100° C.:—

Removed by water.	Yolk soluble in cold distilled water .	32·74	per cent.
	Earthy matter deposited from the above.	26·06	„
Removed by alcohol.	Fatty matter dissolved by alcohol .	8·57	„
	Earthy matter adhering to the fat .	1·40	„
	Wool fibre	31·23	„
		100·00	

Chevreul has here designated as yolk only those impurities which are soluble in cold water, although in the ordinary commercial acceptation of the term it includes all adhering impurities.

According to other observers, the amount of the main constituents of "raw" or "greasy" wool, *i.e.*, just as it comes from the sheep's back, may vary considerably, according to its origin, as follows:—

Moisture	4—24	per cent.
Yolk	12—47	„
Wool fibre	15—72	„
Dirt	3—24	„

As a rule, the finer qualities of wool (*e.g.*, merino) contain more yolk than the coarser.

When wool is washed with water first, as in Chevreul's analysis, not only are certain constituents of a soapy nature removed—*i.e.*, alkaline oleates—but some of the unsaponifiable fatty matter as well, since the oleates cause it to form an emulsion.

A better method of separating these two constituents is first to treat the dried raw wool with ether. This dissolves principally the fatty matter, and although it also takes up as much as ten per cent. of the oleates present, repeated washing of the ethereal solution with water removes the latter almost entirely.

The following substances may thus be distinguished in raw wool—*wool-fat* (soluble in ether), *wool-perspiration* (soluble in water, and partly also in alcohol), *wool fibre, dirt, moisture.*

These may be determined as follows :—

(*a*) Weigh the raw wool, dry it at 100° C., preferably in a stream of some dried inert gas—*e.g.*, hydrogen,—and weigh again. The loss in weight gives the *moisture* present.

(*b*) Extract the dried wool with ether, shake up the ethereal solution with water, in order to remove from it the oleates ; evaporate the separated ether to dryness, and weigh the fatty residue. The weight gives the amount of *wool-fat* present.

Evaporate the separated wash-water to dryness, weigh the residue, and add the weight to that of the portion soluble in water, *i.e.*, the oleates.

(*c*) Wash the ether-extracted wool several times with cold distilled water, and evaporate the solution to dryness. The weight of the residue added to the weight of the oleates dissolved by water from the ethereal solution gives the chief amount of the *alkaline oleates* present. The wool is then washed with alcohol; this always dissolves further minute quantities of oleates, the weight of which must be added to the above. *Earthy oleates* which remain in the wool are decomposed by washing the latter with dilute hydrochloric acid; the acid is removed by washing with water, the wool is then dried, and extracted with ether and alcohol. From the weight of the residue obtained on evaporating the two last solvents to dryness, the amount of *earthy oleates* present in the wool may be calculated. With very dirty wool a good deal of lime is dissolved by the hydrochloric acid, not because of lime soaps but of calcareous dust present.

(*d*) The wool remaining is dried and thoroughly well shaken and teazed out by hand over a large sheet of paper, in order to remove dirt, sand, &c.; care is taken not to lose any of the fibre, the detached particles of which are collected on a fine sieve, and washed with water till free from dirt. The *wool* is dried and weighed; the *sand, dirt, &c.*, are determined by difference.

The following analyses of raw wools give the results obtained by the above method of Märcker and Schulz :—

		Wool of Lowland Sheep.	Wool of full-bred Rambouillet Sheep.	Pitchy Wool.
	Moisture	23·48	12·28	13·28
	Wool-fat	7·17	14·66	34·19
By successive treatment.	Soluble in water (wool-perspiration) . .	21·13	21·83	9·76
	Soluble in alcohol .	0·35	0·55	0·89
	Soluble in dilute HCl .	1·45	5·64	1·39
	Soluble in ether and alcohol . . .	0·29	0·57	—
	Pure wool fibre . .	43·20	20·83	32·11
	Dirt	2·93	23·64	8·38
		100	100	100

35. Wool-fat.—The composition of what is here called *wool-fat* is found to be of a somewhat complicated nature. By treating it with boiling alcohol it may be separated into two portions, the one soluble, the other and larger amount insoluble in this liquid. Further analysis has shown that the soluble portion consists mainly of the alcoholic and fat-like body *cholesterine*, together with *isocholesterine*, each in the free state, and probably also of compounds of both these bodies with such organic acids as acetic acid. The insoluble portion consists essentially of compounds of cholesterine and isocholesterine with oleïc acid, and in lesser amount with solid fatty acids, *e.g.*, stearic acid and hyæna acid.

There seems also to be present in a similar state of combination, but in smaller quantity, some other amorphous body or mixture of bodies, readily fusible, of an alcoholic nature, and containing less carbon than cholesterine. A portion of these various alcoholic bodies, and sometimes also a part of the high atomic fatty acids, are present in the free state.

Wool-fat is certainly not a compound of glycerine, and hence is not a fat as ordinarily understood. This accounts for the difficulty experienced in removing it by mild scouring agents from so-called "pitchy wool," which, as shown in the above analysis, contains it in excessive quantity.

36. Wool-Perspiration. — With reference to the chemical composition of that portion of the yolk which is soluble in water, the *wool-perspiration*, it has been shown by the experiments of Vauquelin, Chevreul, Hartmann, and others, that it consists essentially of the *potassium compounds of oleïc and stearic acids*, and probably also of other fixed fatty acids; it contains further, but in smaller amount, the potassium salts of certain volatile fatty acids (acetic and valerianic acid), potassium chloride, phosphates, sulphates, &c.

Ammonium salts seem to be present in dried extracted yolk in small quantity [equivalent to 0·5 per cent. NH_3]; not sufficient, however, to account for the amount of nitrogen found in yolk (3 per cent.); some other nitrogenous body is evidently present.

As a rule, the wash-water of raw wool has a strong alkaline reaction, since potassium carbonate may be present to the amount of 4 per cent. of the weight of raw wool. Some observers have found it to be entirely absent, in which case, however, it may still be considered to have been secreted by the perspiration glands of the sheep, but to have afterwards acted energetically upon the wool-fat and saponified it, so that while disappearing itself, it has given rise to an increased amount of potash-soaps in the wool-perspiration.

In washing wool on the sheep's back, this potassium carbonate, when present, plays a not unimportant part along with the potash soaps of the yolk, in greatly facilitating the removal of dirt, &c., from the fleece.

Dried extracted yolk contains about 60 per cent. organic matter and 40 per cent. mineral matter (free from CO_2.

The following are two analyses of yolk-ash by Märcker and Schulz :—

Potash . . .	58·94 per cent.	63·45 per cent.
Soda . . .	2·76	trace
Lime . . .	2·44	2·19
Magnesia . . .	1·07	0·85
Ferric oxide . .	trace	trace
Chlorine . . .	4·25	3·83
Sulphuric acid . .	3·13	3·20
Phosphoric acid .	0·73	0·70
Silicic acid . .	1·39	1·07
Carbonic acid . .	25·79	25·34

Yolk-ash consists essentially, therefore, of potash salts, principally carbonates, the carbonic acid arising mainly from the burning of the organic constituents of the yolk.

Maumené and Rogelet give the following analysis, which closely agrees with the above :—

Potassium carbonate	86·78 per cent.
Potassium chloride	6·18
Potassium sulphate	2·83
SiO_2, P_2O_5, CaO, MgO, Al_2O_3, Fe_2O_3, Mn_2O_3, CuO	4·21
	100·00

It is evident from the above that when wool is washed on the sheep's back a considerable quantity of potash is entirely lost to the farmer. It has been estimated that 100 kilos. raw wool yield 8¾ kilos. yolk-ash (free from CO_2), and if the nitrogenous matter and phosphates also washed away are taken into account, it will be seen that the wash-water of raw wool possesses an appreciable manurial value.

37. The Wash-Water Products of Raw Wool.—The great bulk of the wool dealt with in commerce is, however, in the unwashed or "greasy" condition, so that an opportunity is afforded to the woollen manufacturer of extracting the whole of the yolk, and making it serve as a supplementary source of potash.

It is interesting to know that since 1860, and based mainly upon the observations of Maumené and Rogelet, the manufacture of potash salts from the wash-water of raw wool, used in the centres of the French and Belgian woollen industry, has become an accomplished fact, the annual production of potassium carbonate being estimated at about one million kilograms.

After systematically washing the wool with water, the saturated solution is evaporated to dryness. The residue is heated in gas retorts, and the gas evolved may be used for illuminating purposes. The resulting coke is either calcined with access of air or lixiviated with water, and yields crude potassium carbonate. One hundred kilos. "greasy" wool yield 7—9 kilos. crude potassium carbonate, containing 85 per cent. K_2CO_3. The total amount of wool employed for manufacturing purposes in Great Britain in 1884 was 173 million kilos. If the whole of this wool had been treated as above described, it would have yielded over 13 million kilos. of crude potassium carbonate, having a money value of £240,000. It may not be practicable to treat the whole of the wool in this manner, since much of the wool is washed on a comparatively small scale, and central washing establishments would be needed. Much of the wool is washed before importation, so that it might be well for colonial wool-growers to examine this question of the recovery of potash salts from the wash-water of raw wool.

To the agriculturist the question is also of considerable interest, since it is evident that each year there is abstracted from the soil a large amount of valuable constituents. The wool produced in Great Britain alone (60 million kilos.) robs the soil annually of nearly 5 million kilos. of potassium carbonate, which is at present entirely lost to the farmer, who could only replace it at a cost of £84,000.

Another mode of utilising yolk is that recommended by Havrez, according to whom, it is the natural raw material for the manufacture of yellow prussiate of potash. The ordinary method of making this salt is to heat a mixture of crude carbonate of potash, waste animal matter (dried blood, leather clippings, &c.), and iron filings. The resulting fused mass is extracted with water, and on evaporating the solution the desired salt is obtained.

Havrez says that when yolk is submitted to dry distillation it yields a residue, which is an extremely intimate mixture of carbonate of potash and nitrogenous carbon. This residual coke contains, therefore, just the necessary elements for the production of yellow prussiate of potash, and experiment has shown that it gives even a greater yield than the ordinary mixture, containing an equal amount of K_2CO_3, because of the perfect and intimate mixture of the various ingredients.

Havrez has calculated that the money value of the yolk, when used for the production of yellow prussiate of potash, is more than twice that of its ordinary commercial value. He further maintains that when it is used for the simultaneous production of carbonate of potash and yellow prussiate of potash, instead of the former only, there is a gain in value of 50 per cent. For this purpose the dried yolk is mixed with an equal weight of waste animal matter, and heated somewhat longer than usual. Experiment showed that carbonate of potash obtained from 100 kilograms of the residual melt was accompanied by 17·3 kilograms of potassium cyanide, which was capable of yielding 19 kilograms of yellow prussiate of potash.

One hundred kilograms of yolk treated in this manner are said to yield 32 kilograms of carbonate of potash and 4·3 kilograms of yellow prussiate of potash. If these data are correct, what important amounts of these salts might be obtained from this source is seen by the fact that in 1884 England imported from the Australian and Cape colonies, &c., 247 million kilograms of raw wool, containing about 80 million kilograms of yolk. This amount would yield about 25·6 million kilograms of potassium carbonate, valued at £448,000, and about 3·4 million kilograms of yellow prussiate of potash, valued at about £329,000.

Previous to its employment in manufacturing or in dyeing, the raw wool must be thoroughly cleansed from the yolk, but since only a portion is removed by a simple treatment with water, recourse is had to the detergent action of solutions of soap, alkaline carbonates, &c.

No attempt seems yet to have been made in England to collect separately the soluble portion of the yolk for the purpose of recovering the potash salts. The preliminary extraction with water, or steeping, alluded to, is dispensed with by the manufacturer, and the wool is at once washed with the solutions mentioned above. This operation is termed "scouring," and will be treated of in detail in a future chapter; but it may be well to state here that, although in the English method the potash salts are entirely lost, the alkaline and detergent properties of the soluble portion of the yolk are utilised.

CHAPTER IV.

SILK.

38. Origin and Culture of Silk.—Silk differs entirely both from the vegetable fibres and from wool by being devoid of cellular structure. It consists of the pale yellow, buff-coloured, or white fibre, which the silkworm spins round about itself when entering the pupa or chrysalis state.

The numerous varieties of silk may be conveniently divided into two classes, *cultivated* and *wild* silk. The latter is the product of the larvæ of several species of wild moths, which are natives of India, China, and Japan. The former and more important class is produced by the common silkworm, or caterpillar of the moth *Bombyx mori* (Fig. 11), which has become the subject of special culture. The chief seats of the silkworm culture are Southern Europe (including the South of France, Italy and Turkey), China and India.

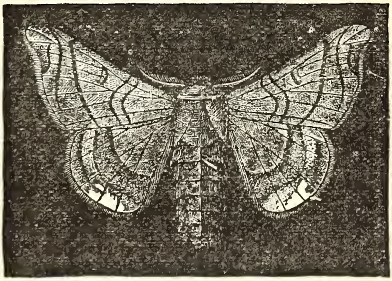


Fig. 11.—Silk Moth (*Bombyx mori*).

The eggs of the European silk moth are about the size and shape of poppy seeds. One gram weight of them contains about 1,350 eggs. They have at first a yellowish colour, which, however, on drying, changes to grey. The rearing of the silkworm is mainly conducted in specially-arranged establishments, called *Magnaneries.* In these, the incubation-chamber is a well-lighted, airy room, where the eggs are spread out on sheets of paper resting on lattice-work. A certain suitable degree of moisture is maintained, and the temperature is gradually raised in the course of about ten or twelve days from 18° C. to 25° C. The young caterpillars, as soon as they appear, are taken to a more roomy chamber, in which there is erected a lath framework strung across with threads and sheets of paper. Here the animals are regularly fed during thirty to thirty-three days, till, indeed, they begin to spin. Their food consists of the leaves of the mulberry tree, *Morus alba*, hence the silk is frequently termed *Mulberry silk.* During the feeding period the silkworm (Fig. 12) increases enormously in size, becoming at length about eight to ten centimetres long and about five grams in weight. As might be expected, such a rapid and enormous development necessitates a frequent renewal of the skin, and moulting takes place three or four times, at tolerably regular intervals of four to six days. On or about the thirtieth day the animal ceases to take food, and evinces a restless activity. At this period it is placed on birch twigs, &c., where it soon begins to spin.

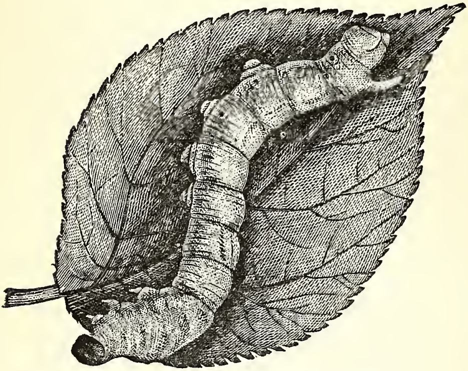


Fig. 12.—Silkworm on Mulberry Leaf.

The silk substance is secreted by two glands symmetrically situated on each side of the body of the caterpillar, below the intestinal canal. Each gland, as shown in Fig. 13, consists of three parts: a narrow tube I C with numerous convolutions, the veritable secreting portion; a central part (C B) somewhat expanded, and constituting the reservoir of the silk substance; a capillary tube B A, connecting the reservoir with a similar capillary canal at A, common to both glands, and situated in the head of the animal, whence issues the silk.

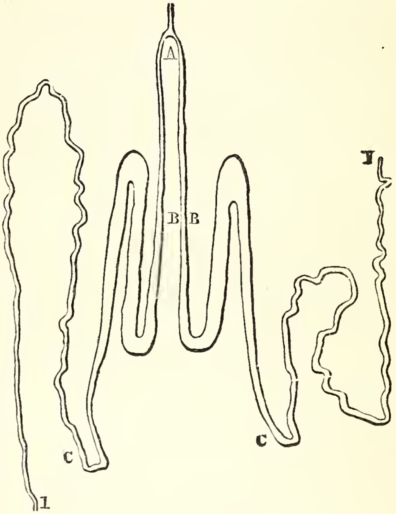


Fig. 13.—The Silk Glands of the Silkworm.

The silk substance as contained in the central reservoir is a clear, colourless, gelatinous liquid. According to Duseigneur, this is surrounded by a layer of another substance, colourless when the silk is white, coloured when it is yellow, and which possibly constitutes the silk-gum to be alluded to subsequently. The whole is enclosed in a thin membrane. A transverse section (Fig. 14) shows that it occupies a space equal to 20—25 per cent. of the total volume, a proportion which corresponds somewhat to the loss sustained by raw silk during the operation of "boiling-off."

Arrived in the capillary tube at A (Fig. 13), the silk substance solidifies, and issues from the spinneret in the form of a double fibre, as represented in Fig. 15. Occasionally the two fibres may be slightly separated at intervals, and form then at these points two transparent solid cylinders.

In the beginning of its spinning operations the silkworm throws round about itself a light scaffolding, as it were, of short fibres connecting the neighbouring points of support. When this is completed its movements become slower, and by moving its head from side to side it gradually forms and lines its dwelling with numerous layers of what may be termed silken lattice-work.

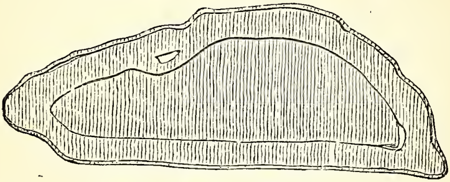


Fig. 14.—Section of Silk-bag.

Towards the interior the layers become firmer and denser, while the innermost one, which immediately protects the animal, forms a thin parchment-like skin. The egg-shaped product is called a *cocoon* (Fig. 16). It is made up of a double fibre, only rarely broken, varying in length from 350 to 1,250 metres, and with a diameter of about 0·018 millimetre. Each fibre is thickest in the outermost portion of the cocoon, and becomes thinner

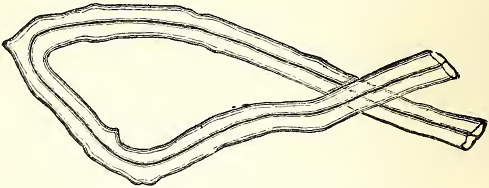


Fig. 15.—Microscopic Appearance of Raw Silk Fibre.

towards the interior, owing to the exhaustion of the caterpillar from want of food during the spinning process.

The cocoons are white or yellow, contracted in the centre, about 3 centimetres long, and 1·5—2 centimetres thick.

As soon as the metamorphosis of the caterpillar into the chrysalis state is completed, the cocoons are collected. Those which are intended for breeding purposes are left to themselves in a room heated to 19°—20° C. Three weeks after the spinning of the cocoon, the silk moth, which has now been formed in the interior, emits a peculiar kind of saliva; with this the animal softens one end of the cocoon, and pushes its way out. A few days after the females have laid their eggs they die, not being provided with any organ of nutrition. The eggs are slowly dried, and stored in glass bottles in a dry dark place till the following spring.

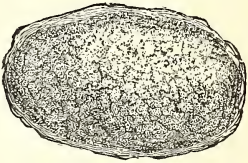


Fig. 16.—Silk Cocoon.

Experience has shown that the worms issuing from 100 grams of eggs consume 3,500—5,000 kilograms of leaves, and produce, under favourable conditions, 87,900—117,200 cocoons, weighing 150—200 kilograms, and these yield 12—16 kilograms of reeled silk.

In their natural state cocoons contain generally :—

Moisture	68·2 per cent.
Silk	14·3 ,,
Floss (*bourré*) . . .	0·7 ,,
Chrysalis	16·8 ,,

The good silk is obtained from those cocoons of which the pupæ are killed, either by heating the cocoons for two to three hours in an oven heated to 60°—70° C., or by means of steam. The latter method is the more general, the apparatus consisting essentially of a boiler for generating the steam, and a steam-box in which the cocoons are placed. When subjected to steam, the pupæ are killed in ten or twelve minutes.

The external loose flossy silk is first removed, and the cocoons are thrown into baskets, which are then placed in the steaming-box. When taken out, the cocoons are put between woollen blankets, so that the heat may be retained and its effect continued a little longer. After a few hours they are spread out on tables, and shovelled about till perfectly dry. This last operation is specially requisite with such cocoons as cannot be reeled off at once. Although the killing of the cocoons by steam has the great advantage that there is no fear of the silk itself being damaged by overheating, still it has certain defects. The most serious are, that some of the pupæ burst and soil the silk, and that the fibres soften somewhat, and tend to stick together, rendering the subsequent reeling more difficult.

After killing, the cocoons are "sorted," or divided into classes of different quality. In every piece of woven silk the warp threads have to bear the greatest strain, and, as a rule, must appear on the surface of the fabric, hence the best cocoons are chosen for the warp, since they must yield strong, smooth, even, and lustrous fibres. These fibres, too, in the subsequent process of reeling, are manipulated somewhat differently from the weft-fibres. The product of this choice and particular treatment forms the best quality of silk, *i.e.*, warp-silk, which is known as *Organzine*. A somewhat inferior class of cocoons is worked up to form weft-silk, or *Tram.*

39. **Raw Silk.**—In the *reeling* process a number of cocoons (4—18) are thrown into a basin of warm water, in order to soften the gummy envelope of the fibres, thus permitting their ready separation from the cocoon, and also to cause the subsequent agglutination of whatever number of fibres may be thrown together to form a single thread. During this reeling process two threads, composed of an equal number of fibres, are passed separately through two perforated agate guides; after

being crossed or twisted together at a given point, they are again separated, and passed through a second pair of guides, thence through the distributing guides on to the reel. The object of this temporary twisting or crossing (Fr. *croissage*) is to cause the agglutination of the individual fibres of each thread, and to aid in making the latter smooth and round.

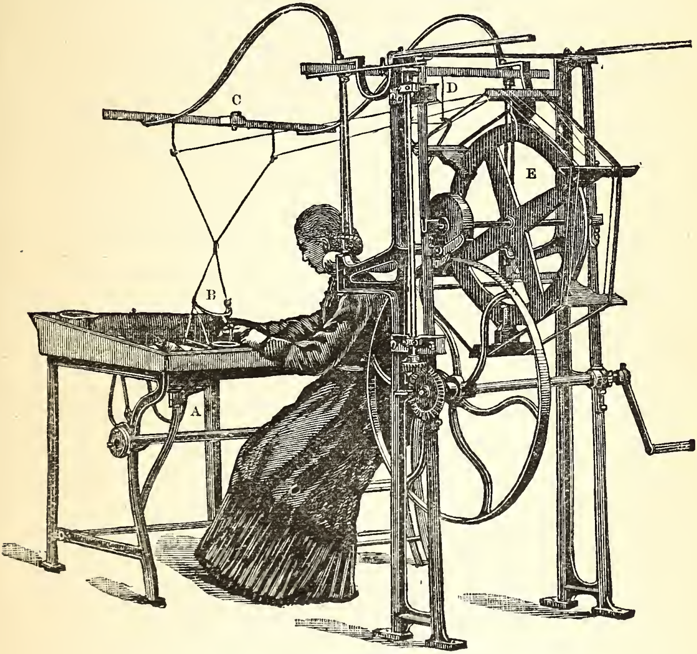


Fig. 17.—Silk-reeling Machine.

Fig. 17 shows a silk-reeling machine as used in Italy and Southern France. The following are the principal parts: A, a tinned copper basin of hot water, containing the cocoons for reeling: it is heated either by steam or by means of a stove; B, "filières," or perforated agate discs, through which pass the several fibres destined to form a raw-silk thread; C, a "croiseur," used for the purpose of crossing the fibres together; D, a guide which moves slightly from side to side, and distributes the silk on the reel to prevent the threads from sticking to each other; E, the reel proper, which is made to revolve and wind the silk from the cocoons. The unequal diameter of each fibre at different portions of its length is taken into account by the reeler when introducing new fibres into the thread to replace those which have run out. The quality of raw-silk depends very much indeed upon the care bestowed on the reeling process.

The loss through removal of the external floss (*bourre*) varies from 18 to 30 per cent., according to the cocoons and the care bestowed by the worker.

Reeled-silk, or *raw-silk*, as it is generally termed, constitutes the raw material of the English silk manufacturer. Before being used for weaving, two or more of the raw-silk threads are "thrown" together and slightly twisted by the silk spinner, or "throwster," and in this way the various qualities of Organzine and Tram—also embroidery-sewing silks, &c.—are produced.

A very brief description of the operations involved may suffice. The preliminary processes of "winding" and "cleaning" are followed by that of "doubling," which simply consists in placing two threads ("singles") side by side, and winding them together without twist. The so-called "spinning" of silk consists merely in twisting the threads either before or after doubling.

The "Tram," already alluded to, is the product of the union of two or more single untwisted threads, which are then doubled and slightly twisted.

"Organzine" is produced by the union of two or more single threads separately twisted in the same direction, which are doubled and then re-twisted in the opposite direction.

40. **Waste-silk** is that which proceeds from perforated

and double cocoons, and such as are soiled in steaming; also the extreme outer and inner portions of the cocoon: in short, all silk obtained from cocoons in any way soiled or unable to yield a continuous thread. The killed chrysalides can be used as a source of oil, and the residue after extraction may serve for manure.

All such waste-silk materials are washed, boiled with soap, and dried. They are afterwards carded and spun like cotton, and yield the so-called *Spun silk*. *Schappe silk* is a similar product, made from waste silk without previous boiling.

Careful examination of the perforated cocoons has revealed the fact that their fibres are not discontinuous. The moth does not eat its way out of the cocoon, but rather pushes aside the previously softened fibres. Attempts made to reel these cocoons by the ordinary methods have failed, since the cocoons soon fill with water and sink. The problem of causing the cocoons to float is said to have been recently solved by introducing small india-rubber cells in a compressed state, and then blowing them out.

41. **Wild Silk.**—Of "wild silks," the most important is the *Tussur* silk (Hindustani, *Tusuru*, a shuttle), also called Tusser, Tasar, Tussore, and Tussah. It is the product of the larva of the moth *Antheræa mylitta.*

The Tussur moth is found in nearly all parts of India, where it seems to feed on a large variety of plants. In some districts it is reared by the natives. The cocoons, which are much larger than those of *Bombyx mori*, are egg-shaped and of a silvery drab colour. They are attached to the twigs of the food-trees by a peduncle having a terminal ring. The outer silk is somewhat reddish, and consists of separate fibres of various length, while the rest is generally unbroken to the centre of the cocoon. The cocoon is extremely firm and hard, the fibres being cemented together by a peculiar secretion of the animal, which permeates the whole wall of the cocoon, and imparts to it its drab colour.

Tussur silk is used for the manufacture of the well-known drab or buff-coloured Indian silks. The cocoons are boiled and carded, or even reeled, although this latter process presents difficulties. Silk plush is largely made from carded Tussur silk.

Other wild silks are, *Eria silk*, from *Attacus ricini; Muga silk,* from *Antheræa assama; Atlas silk,* from *Attacus atlas; Yama-maï silk,* from the *Antheræa yama-maï* of Japan, &c.

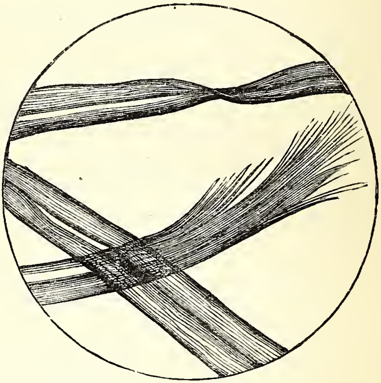


Fig. 18.—Microscopic Appearance of Tussur Silk Fibre.

Under the microscope a raw mulberry-silk fibre appears as a double fibre (Fr. *bave*) consisting of two solid structureless cylinders (Fr. *brin*), more or less united together (Fig. 15); after "boiling-off" with soap, however, this double fibre separates into a pair of distinct fibres, having a more or less irregular, somewhat rounded triangular section.

Wild silk is distinguished from mulberry silk by the longitudinal striations seen in each of the double fibres when under microscopic examination (Fig. 18), and by the apparent contraction of the fibre at certain points. The former are due to the fact that the wild-silk fibre is composed of a large number of fibrils, while the latter appearance is seen because the more or less flattened fibres are twisted at the contracted points.

42. Physical Properties.—The most important physical properties of silk are its lustre, strength, and avidity for moisture.

One other distinctive property which it possesses in certain conditions is that of emitting a peculiar crisp, crunching sound (Fr. *cri*), *e.g.*, when a bundle of silk yarn is tightly twisted and pressed together. This peculiar property is called the "scroop" (Fr. *craquant*) of the silk, and no doubt gives rise to the rustling noise heard when two pieces of silk fabric rub lightly against each other.

The intensity of the phenomenon varies with the nature of the dyeing and mechanical processes adopted, with the diameter and twist of the threads, &c.

The property is absent in raw-silk and in "boiled-off," or in "souple" silk; it is only manifested if the last bath or solution through which the silk has passed contained an acid salt or free acid. Silk which has been worked in a neutral or alkaline bath—*e.g.*, a soap bath—possesses no "scroop." No sufficient explanation of the action of acid in producing scroop has been given, but it is not improbable that acids cause the fibres to become more rough or irregular on the surface, so that when submitted to pressure they slip past each other with a jerky movement.

When it is desired to impart scroop to the silk after dyeing, it is submitted to a special treatment. Very often it is first passed through a weak soap bath or an oil emulsion, and then into a weak acid bath, or it is introduced into a bath which is both oily and acid. (*See* Black Silk Dyeing, p. 337.)

In order to develop all the qualities of softness and brilliancy of which silk is capable, it is submitted (while

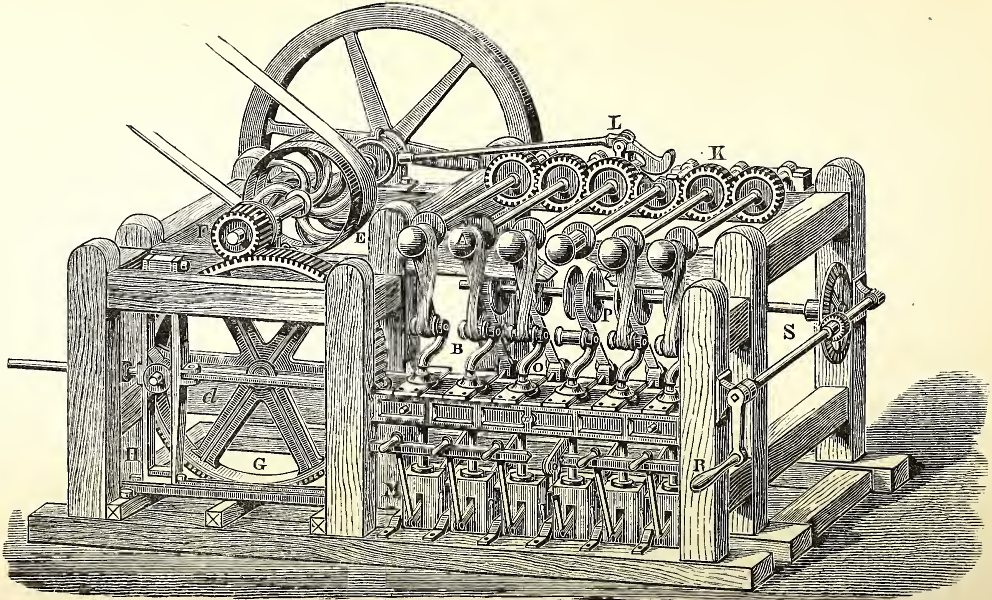


Fig. 19.—Stringing Machine for Silk.

still in the form of hanks of yarn) to the following mechanical operations :—

43. **Shaking Out** (Fr. *sécouage*).—The object of this is to open out or beat out the hanks of silk, and to give the latter a uniform appearance by removing all tendency to curl or wrinkle. It is generally performed after drying, but if before, the drying is greatly facilitated. It consists in hanging the hank of yarn on a strong smooth wooden peg fixed to the wall, and inserting a smooth wooden rod in the loop, which is then vigorously and quickly pulled. The point of suspension is frequently changed, and the shaking out is repeated. The operation may also be done by a machine of M. César Corron, St. Etienne, with the utmost regularity.

44. **Stringing or Glossing** (Fr. *chevillage*).—This operation, which was originally only performed in conjunction with the "shaking-out" for the purpose of straightening the threads, and dressing the hanks after diverse operations of the dye-house, has now acquired increased importance, particularly in the case of souples. With these it forms the final operation, the silk being operated upon in the dry state. Its object in this case is to complete the separation of the double silk fibre into its constituent fibres, and to add lustre.

The operation consists in twisting the hanks of silk when perfectly dry. They are hung on pegs, as in the last operation, which it generally succeeds. A stated and progressive tension is thus given, which adds softness and brilliancy to the fibres. This operation can also be performed with a machine, a representation of which is given in Figs. 19 and 20.

The stringing machine (Fig. 19) is composed of a series of horizontal pegs A, which can be made to revolve by means of the lever and ratchet L and the cog-wheels K. A second series of horizontal rollers B, situated directly beneath the pegs A, are fixed on elbow-shaped spindles. They are capable of two movements, namely, that of revolving on their own axis—*i.e.*, the horizontal axis of the elbow—as loose pulleys, and also at right angles to this, by the revolution of the vertical spindle of the elbow. This last movement is caused as follows: Each spindle is supported by a collar on a box U, enclosing a cog-wheel, which is revolved by a ratchet; this is actuated by the backward and forward movement of the horizontal arm *d* imparted by the frame H, through the medium of the cog-wheels F and G and the pulley E.

Each spindle is also capable of sliding up and down. Attached to the bottom of the roller-pegs B (Fig. 20) are the weights C, which can either be raised separately by the jointed levers M pressing against the pulley V, or all together by means of the handle R. When this handle is turned, the cog-wheels S cause the pulley P to revolve, the counterpoise O descends, and the weights C, together with spindles and roller pegs B, are raised.

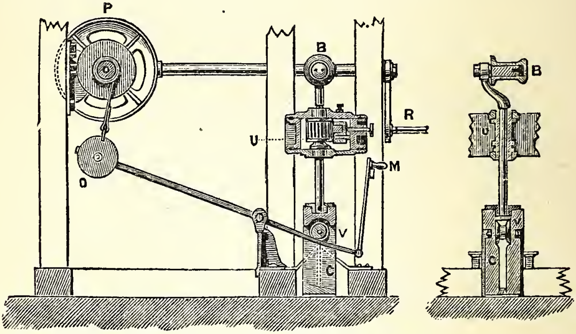


Fig. 20.—Details of Silk-Stringing Machine.

Suppose now the hanks of silk are slung over the pegs A and B; by the action of the ratchet and lever D the roller pegs B revolve and the hanks are twisted, the pegs, weights, &c., being at the same time raised by the shortening of the hanks. Automatically the movement of the lever *d* is reversed, the hanks untwist, and are kept in the stretched condition by the descending weights. At a given moment, namely, just when the hanks are entirely untwisted, the lever L comes into play, and causes a slight rotation of the pegs A, so that the hanks become suspended in a fresh position, to be again twisted by the action of the lever *d*. The whole of the movements are automatic, and by a few repetitions of this twisting, untwisting, and displacement of the hanks, the operation is complete.

In some cases (*e.g.*, with sewing silks), stringing consists simply in twisting the hanks of silk as tightly as possible, then placing the peg in a locked position, and leaving the hanks in this tightly twisted condition for several hours. The operation may be repeated frequently during from ten to fifteen days. Its object is to give increased lustre.

45. Silk Lustreing. — This operation, effected by means of the machine represented in Fig. 21, serves to impart the maximum of brilliancy to the fibre. It also facilitates the subsequent winding. The dyed and dried, or sometimes incompletely dried, silk is submitted to a gentle stretching between two polished steel rollers, C and D, revolving in the same direction, and enclosed in a cast-iron box, the lid A and side B of which can be rapidly removed when necessary. During the rotation of the cylinders, steam at a moderate pressure is allowed to enter. The stretching is effected by drawing the roller C away from D by means of the hook F, actuated by the cog-wheels at E.

The brilliant mother-of-pearl lustre possessed by silk undoubtedly gives it the place of honour among all textile fibres.

46. Tenacity and Elasticity of Silk.—The specific gravity of silk is 1·367. Its tenacity and elasticity are remarkably great. The former is said to be little inferior to that of a good quality of iron wire of equal diameter, while the latter is such that a silk fibre can be stretched $\frac{1}{7}$ — $\frac{1}{5}$ of its original length without breaking. These properties are taken advantage of in the operations of shaking out, stringing, and lustreing, as described above. The finest silk is proportionally the strongest and most tenacious. Damp silk is less tenacious and more elastic than dry silk.

If perfectly dried silk is wetted with water, it contracts about 0·7 per cent., and still more if the water contains mineral or organic substances which penetrate the fibre and cause it to swell up. These effects take place during the various operations of dyeing; hence the necessity of stringing, stretching, and lustreing, above alluded to, in order to prevent or counteract the contraction.

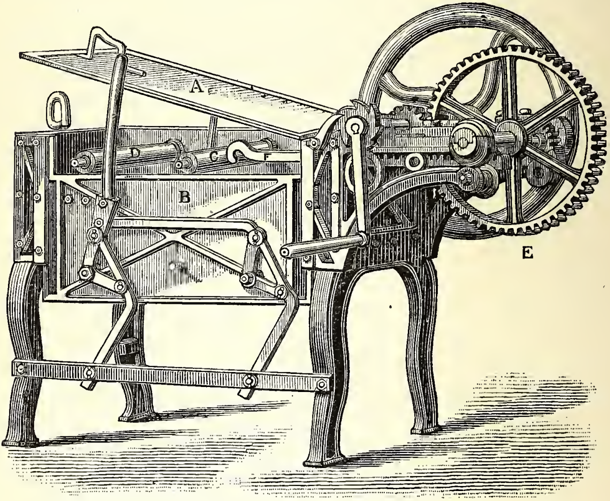


Fig. 21.—Silk-lustreing Machine.

The tenacity and elasticity of raw-silk reside largely in its external coating of silk-glue. By boiling-off with soap, it loses 30 per cent. of its tenacity, and 45 per cent. of its elasticity.

These properties vary in weighted silk, according to the nature of the weighting. If the fibre is simply coated with such substances as gelatin, albumen, starch, &c., the tenacity will be as a rule increased, but if the weighting materials employed penetrate the substance of the fibre, and cause it to swell in a greater or less degree, the natural properties of the silk will be modified accordingly. Some agents, like the simple colouring matters, have no appreciable influence, while others, *e.g.*, astringents and metallic salts, when used in large excess, gradually destroy the valuable properties of silk entirely. (*See* Black Silk Dyeing, p. 332.)

If silk is heated to 110° C. it loses all its natural moisture, but remains otherwise quite unchanged. Exposed to 170° C., and higher, it soon begins to decompose and carbonise. If a silk fibre be inserted in a flame it has the appearance of fusing like wool, but it does not give off quite such a disagreeable odour.

Silk is a very bad conductor of electricity, and since it readily becomes electric by friction, this condition, once acquired, is very persistent, and is apt to become a source of trouble during the mechanical operations involved in manufacturing. The most effective mode of overcoming the difficulty is to keep the atmosphere of the workrooms in a suitable state of humidity.

In its boiled-off and pure state silk resists ordinary decay most thoroughly, and it is rarely attacked by insects.

47. Silk Conditioning.—If raw silk be kept in a humid atmosphere it is capable of absorbing thirty per cent. of its weight of moisture without this being at all perceptible. This circumstance, coupled with the high price of raw silk, makes it of very great importance to those who trade with it to know exactly what weight of normal silk there is in any given lot which may be the subject of commercial dealings. To ascertain this information there have been established, in about thirty-seven centres of the silk industry, so-called

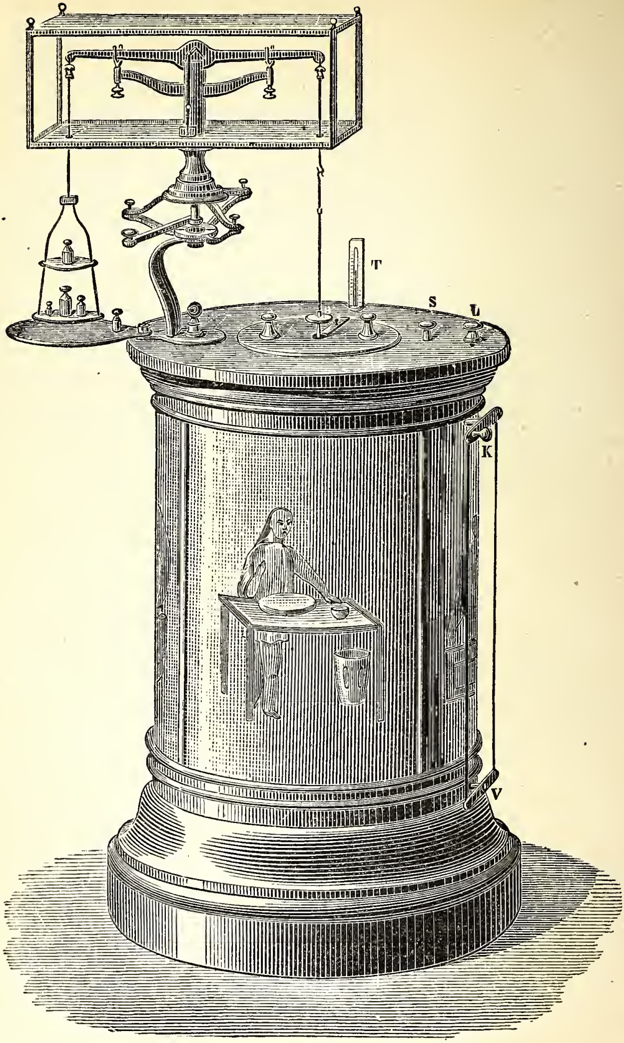


Fig. 22.—Conditioning Apparatus.

conditioning establishments, *e.g.*, in Lyons, Crefeld, Zurich, Bâle, Turin, Milan, Vienna, Paris, London, &c., &c.

Fig. 22 shows the external appearance of the essential apparatus of such an establishment, namely, the desiccator. It consists of an enamelled cylindrical hot-air chamber. One arm of a fine balance sustains a crown of hooks, to which are attached the skeins of silk to be dried. The suspending wire passes through a small opening in the cover of the cylinder. The other arm of the balance carries the ordinary pan for weights.

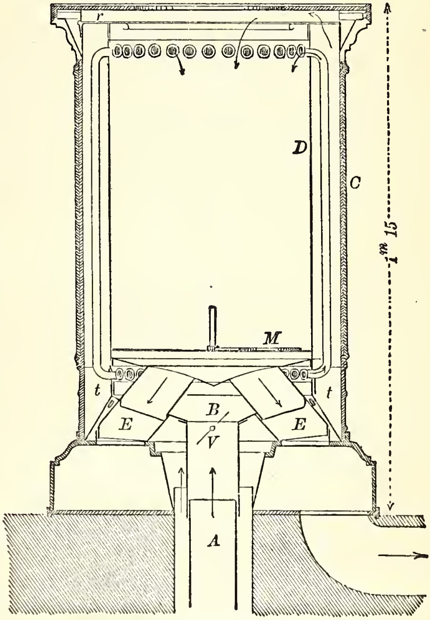


Fig. 23.—Section of Conditioning Chamber.

Fig. 23 gives a vertical section of the chamber. Hot air at 110° C. enters by the tube A from a stove situated in a cellar below, passes into the space B, and thence by thirty-two vertical tubes, *t*, placed between the two concentric cylinders C and D, it enters the upper portion of the inner cylinder D. The hot air descends, dries the silk, and escapes by the tubes E, which communicate with the exit flue. The apparatus is provided with a valve V, actuated by the lever K (Fig. 22) for regulating or shutting off the current of hot air.

The air which passes outside the brickwork of the stove, and is thus heated only to a moderate degree, passes upwards between the cylinders C and D into the space *r;* by means of the button L, which actuates a slide-valve, its entrance into the central chamber can be regulated. By means, therefore, of the lever K and the button L, the supply of hot and cold air into the central chamber can be regulated to a nicety, and the temperature of the mixture is ascertained by the thermometer T. The button S actuates the valve M, which cuts off communication with the exit flue and stops the current of air during a final weighing operation.

Several hanks of silk are taken from the bale to be tested and divided into three lots, in order to be able to make two parallel determinations, and a third if necessary. The weight is first rapidly taken, under ordinary circumstances, on a fine balance; the hanks are then suspended in the desiccator and counterpoised, and the hot air current is allowed to circulate till no further loss of weight takes place. One operation may last from a half to three-quarters of an hour.

The average loss of weight usually met with is about 12 per cent. Absolutely dry silk is not reckoned as the standard article, but such as contains about 90 per cent. dry silk and 10 per cent. moisture. The legal weight is really obtained by adding 11 per cent. to the dry weight.

48. Chemical Composition.—The silk fibre has been the subject of numerous chemical researches, the general result of which may be summed up by saying that it is composed essentially of two distinct parts: first, that constituting the central portion of the fibre, and secondly, a coating, or envelope, consisting apparently of a mixture of substances mostly removable by hot water, or, at any rate, by solvents which have little or no action on the central portion.

Fibroïn.—In order to determine the character and amount of these several substances, Mulder submitted raw Italian silk to the successive action of boiling water, alcohol, ether, and hot acetic acid, and in this way obtained in a comparatively pure state the central silk substance, to which he assigned the name *Fibroïn.* The following numbers give the results of his analysis :—

	Yellow Italian silk.	White Levant silk.
Silk fibre (fibroïn) . . .	53·35	54·05
Matters soluble in water . .	28·86	28·10
,, ,, alcohol . .	1·48	1·30
,, ,, ether . .	0·01	0·05
,, ,, acetic acid .	16·30	16·50
	100·00	100·00

By a further examination of the substances which each solvent had extracted, he arrived at the following more detailed analysis :—

	Yellow Italian silk.	White Levant silk.
Fibroïn	53·37	54·04
Gelatin	20·66	19·08
Albumen	24·43	25·47
Wax	1·39	1·11
Colouring matter	0·05	0·00
Resinous and fatty matter . .	0·10	0·30
	100·00	100·00

Mulder explains that on evaporating the aqueous solution to dryness, the residue would not entirely redissolve in water. This insoluble portion, therefore, and that which is dissolved by acetic acid, has been reckoned as albumen. Exception has been taken by Bolley with regard to the presence of this albumen, for if it is borne in mind that the temperature employed in killing the cocoons, and that of the water used during the reeling process, is such as to coagulate any albumen which might possibly be present; it is highly improbable that raw silk would contain any soluble albumen.

Further, it has been shown that living cocoons, which have not therefore been submitted to any steaming process, but have simply been opened and heated with tepid water, contain *no* albumen. Fibroïn itself, too, is known to be somewhat soluble in strong acetic acid, so that it may, on the whole, be concluded, that what Mulder found to be soluble in acetic acid was not albumen, but altered fibroïn, and that the percentage of this latter substance in silk which he gives, is too low.

By heating raw silk for several hours with water at 133° C., a residue of fibroïn is obtained which, after the removal of fatty matter by ether, and colouring matter by alcohol, represents 66 per cent. of the weight of the silk. Even this figure may possibly be too low, since the usual loss in practice during the operation of "boiling-off" is 25-30 per cent.

The percentage composition of pure *Fibroïn* has been variously stated, probably owing to the different hygrometric state of the fibres examined. Cramer gives the formula as $C_{15}H_{23}N_5O_6$.

Sericin.—That portion of silk which is soluble in warm water can be precipitated from its solution by lead acetate. By submitting this precipitate to a somewhat tedious series of operations—such as washing with water, suspending in water and decomposing with sulphuretted hydrogen, filtering, and evaporating the filtered solution, precipitating and extracting with alcohol, then with ether—it is possible to obtain the essential constituent of the external envelope of the silk fibre as a colourless, odourless, tasteless powder. It swells up in cold water, and is somewhat more soluble in hot water than gelatin. A six per cent. solution of it gelatinises on cooling, and its solutions are precipitated by alcohol, tannic acid, and metallic salt solutions. Altogether, its physical and chemical properties are very similar to those of glue and gelatin; hence *Sericin* is often called *silk-glue*, sometimes also *silk-gum*. Its chemical composition is represented by the formula—$C_{15}H_{25}N_5O_8$.

It is distinct from ordinary glue, however, according to some observers, since when boiled with dilute mineral acids it yields different products.

If the formulæ given for fibroïn and sericin be compared, a relationship is apparent which may be expressed by the following equation :

$$\underset{\text{Fibroïn.}}{C_{15}H_{23}N_5O_6} + O + H_2O = \underset{\text{Sericin.}}{C_{15}H_{25}N_5O_8}$$

Although these formulæ can only be considered as representing approximately the percentage composition of these two bodies; the above comparison has been taken by some as an indication that originally, *i.e.*, at the moment of secretion, the silk fibre is probably a homogeneous substance, which, by the action of the air and moisture, rapidly becomes altered superficially. This view is supported by the observation that if moist fibroïn be left exposed to the air for a lengthened period it becomes partially soluble in water. Bolley and Rosa have found also that the silk-bags taken from living worms are composed almost entirely of fibroïn, since only 1·7 per cent. is soluble in boiling water, and the elementary analysis is consistent with the formula of fibroïn. The physiological studies of Duseigneur, and especially his examination of the transverse section of the silk-bag, already alluded to, appear to contradict this view.

Influence of Reagents on Silk.

In contact with various liquids silk not only absorbs them rapidly, on account of its great porosity, but sometimes retains them with extreme tenacity ; this is the case, *e.g.*, with alcohol and acetic acid. For the same reason it has great aptitude for fixing mordants and colouring matters.

49. Action of Water.—Prolonged boiling with water removes from raw silk its silk-glue, but it has little effect upon the fatty, waxy, and colouring matters present. The tenacity of the fibre is reduced even more than by the ordinary methods of ungumming with soap solutions. A similar solvent action is exercised by all liquids; for this reason it is not customary to mordant silk with hot solutions, and the dyeing is conducted at a temperature as low as circumstances will permit.

50. Action of Acids.—Speaking generally, concentrated mineral acids rapidly destroy silk, but if sufficiently diluted their action is insensible. Warm dilute acids, however, dissolve the sericin of raw silk, and hence these may be used in ungumming (soupling). Concentrated *sulphuric acid* dissolves silk, giving a viscous brown liquid; on diluting the latter with water a clear solution is obtained, from which the fibroïn is precipitated on the addition of tannic acid.

Concentrated *nitric acid* also rapidly destroys silk; but if diluted, the latter is only slightly attacked and coloured yellow, in consequence of the formation of xanthoproteïc acid. This reaction is made use of in distinguishing silk from vegetable fibres. Formerly it was also utilised in dyeing; a method, however, not to be commended, since the colour is produced at the expense of the silk itself, which must inevitably be weakened by the process.

Hydrochloric acid, if applied in the gaseous state, destroys the fibre without liquefying it, but a concentrated aqueous solution readily dissolves it. Hydrochloric acid 38° Tw. (Sp. Gr. 1·19) when applied cold, dissolves an equal weight of silk without even then being saturated. Dilute hydrochloric acid has no sensible action, except upon the sericin of raw silk, which it more or less removes.

Phosphoric and *arsenic acids* in dilute (5 per cent.) aqueous solution act like other weak acids in removing the sericin from raw silk, and have been proposed as ungumming agents instead of soap, but they are not used in practice.

Permanganic acid, either in the free state or in combination with potassium, acts energetically on silk;

it oxidises and colours the fibre brown by deposition of hydrated manganic oxide. If this be removed by immersion in a solution of sulphurous acid, the silk is left in a remarkably pure white condition. Although recommended on this account for bleaching silk, it is not altogether suitable, since the silk thus bleached always has a tendency to become yellowish under the influence of alkalis.

Sulphurous acid is used in bleaching silk.

Chromic acid and chromates, like permanganic acid, oxidise silk, leaving the fibre of a pale olive tint.

The action of *organic acids* on silk has been little studied; it varies, no doubt considerably, according to their concentration, temperature, &c.

Hot dilute organic acids remove the sericin from raw-silk but do not affect the fibroïn much. Cold glacial acetic acid removes the colouring matter from yellow raw-silk without dissolving the sericin. Silk is entirely dissolved when heated under pressure with acetic acid.

51. Action of Alkalis.—Concentrated solutions of *caustic soda* and *potash* rapidly dissolve raw-silk, especially if applied warm.

Caustic alkalis, sufficiently diluted so as not to act appreciably upon the fibroïn, will dissolve off the sericin, and have been tried as ungumming agents. For ordinary use, however, they must be avoided, since the silk is always left impaired in whiteness and brilliancy.

Pure *ammonia* solution, even if used warm, has no sensible action on boiled-off silk, but if it is at all impure the silk becomes dull and dirty from absorbed tarry matter. Ammonia seems to favour the absorption by silk of salts of calcium, magnesium, &c.

Alkaline carbonates act like the caustic alkalis, but in a less energetic manner, and they are not employed as ungumming agents. Of all alkaline solutions, those of *soap* have the least injurious effect. When used hot, they readily remove the sericin from raw-silk, and leave the fibroïn lustrous and brilliant; hence soap is *par excellence* the ungumming agent employed. *Borax* acts somewhat like soap, but cannot replace it in practice.

If raw silk be steeped for twenty-four hours in clear, cold *lime-water*, it swells up considerably, the lime seeming to have a strong softening action on the sericin; when this is removed by dilute acid and a subsequent soap bath, the fibroïn seems not to have suffered otherwise than by the loss of its natural brilliancy. Prolonged contact, however, with lime-water renders silk brittle and disorganised.

Chlorine and hypochlorites attack and destroy silk rapidly, and cannot be used as bleaching agents. Applied in weak solutions, with subsequent exposure of the fibre to the air, they cause the silk to have an increased attraction for certain colouring matters.

52. Action of Metallic Salts.—If silk is steeped in cold solutions of several metallic salts, *e.g.*, of lead, tin, copper, iron, aluminium, &c., it absorbs and even partly decomposes them, so that less soluble basic salts remain in union with the fibre. The methods of mordanting silk with aluminium, tin, and iron salts depend upon this fact. Sometimes, as in the case of ferric and stannic salts, the quantity of basic salt which may be precipitated on the fibre is sufficient to serve as weighting material.

Concentrated zinc chloride, 138° Tw. (Sp. Gr. 1·69), made neutral or basic by boiling with excess of zinc oxide, dissolves silk, slowly if cold, but very rapidly if heated, to a thick gummy liquid. This reagent may serve to separate or distinguish silk from wool and the vegetable fibres, since these are not affected by it. If water be added to the zinc chloride solution of silk, the latter is thrown down as a flocculent precipitate. If this is washed free from zinc salt and dissolved in ammonia, it is said that the solution may serve to cover cotton and other vegetable fibres with a coating of silk substance. Dried at 110°—115° C., the precipitate acquires a vitreous aspect, and is no longer soluble in ammonia.

An ammoniacal solution of cupric hydrate dissolves silk, the solution not being precipitated by neutral salts, sugar, or gum, as is the case with the analogous solution of cotton. An ammoniacal solution of nickel hydrate also dissolves silk.

A most excellent solvent for silk is an alkaline solution of copper and glycerine, made up as follows: dissolve 16 grams copper sulphate in 140 — 160 c.c. distilled water, and add 8 — 10 grams pure glycerine (Sp. Gr. 1·24); a solution of caustic soda is dropped gradually into the mixture till the precipitate at first formed just re-dissolves; excess of $NaOH$ must be avoided. This solution does not dissolve either wool or the vegetable fibres, and may serve therefore as a distinguishing test.

53. Action of Colouring Matters. — Generally speaking, silk has a very great affinity for the monogenetic colouring matters. It can be dyed direct with the aniline colours, for example, with the greatest facility. It has, however, little attraction for mineral colouring matters.

An examination of sections of dyed silk reveals the fact that the colouring matter (or the mordant) penetrates the substance of the silk fibre to a greater or less degree, according to the solubility of the colouring matter, the duration of the dyeing process, and the temperature employed. If the silk is dyed only for a short time, a section of the fibre shows an external concentric zone of colour, while if the dyeing operation is continued sufficiently long, it is coloured right to the centre. If a mixture of two colouring matters be applied, either simultaneously or successively, both are absorbed, the more soluble, or that which has been allowed to act longest, penetrating the fibre most deeply. Externally a mixed effect is produced in this case, but a section of the fibre reveals in most cases two concentric zones of colour. Silk thoroughly mordanted with a ferric salt presents in section a uniform yellow tint; if dyed subsequently in an acidified solution of potassium ferrocyanide, the ferric oxide deposited in the silk gives place to Prussian blue, at first in the outer portions only, but by degrees even in the centre, especially if the temperature of the bath be raised. A similar effect is produced if a bath of tannin be substituted for that of potassium ferrocyanide. It is indeed difficult to say what number of substances might be successively absorbed by the silk, and penetrate it either by juxtaposition or by reacting upon each other.

The action of colouring matters on *raw* silk is similar; but in many cases, *e.g.*, in the black dyeing of souples, the colouring matter is situated principally in the external silk-glue, which, becoming brittle through the large amount of foreign matter it then contains, breaks up and assumes the form of microscopic beads.

OPERATIONS PRELIMINARY TO DYEING.

CHAPTER V.

COTTON BLEACHING.

54. Object of Bleaching.—As already noticed in treating of the cotton fibre, raw cotton is contaminated with several natural impurities, and although these are comparatively small in amount, they impair the brilliancy of the white belonging to pure cellulose. Hence cotton yarn as it leaves the spinner has invariably a soiled or greyish colour. When such yarn is woven it is still further contaminated with all the substances (amounting sometimes to 30 per cent.) which are introduced during the sizing of the warps, *e.g.*, china clay, grease, &c.

Bleaching consists in the complete decolorising or removal of all these natural and artificial impurities, either for the purpose of selling the goods in the white state, or in order to make them suitable for being dyed light, delicate, and brilliant colours.

55. Bleaching of Unspun Cotton (Cotton-wool). —Although cotton-wool is now largely dyed, it is seldom or never bleached in this form, because it would become more or less matted together. As a rule, the only treatment previous to dyeing which it receives is that of boiling with water until thoroughly wetted. It would no doubt be better to boil with a dilute solution of caustic or carbonated alkali, and afterwards to wash well with water —*e.g.*, in machines similar to those used in loose-wool scouring (*see* p. 100)—since by this means the natural waxy matters, &c., would be more thoroughly removed. More complete bleaching would be tedious, and is probably unnecessary.

56. Bleaching of Cotton Yarn.—When cotton yarn has to be dyed black or dark colours, it is as a rule not bleached, but merely boiled with water till thoroughly softened and wetted. For light colours the dyer frequently effects a rapid, though perhaps more or less incomplete bleaching, by passing the wetted yarn (*e.g.*, warps) through a boiling weak solution of soda-ash, then steeping it for a few hours in a cold weak solution of chloride of lime or hypochlorite of soda. It is then washed in water, steeped in dilute hydrochloric acid, and finally well washed.

A more complete and thorough bleaching is that effected by the operations now to be briefly described.

"Warps" are loosely plaited by hand or machine, in order to reduce their length. If the yarn is in hanks it is either retained in that form, or linked together to form a chain, the latter being the better and more economical method.

1. *Ley boil.*—For 1,500 kilos. yarn, boil six hours with 2,000 litres water and 300 litres caustic soda 32° Tw. (Sp. Gr. 1·16); steep in water for forty-five minutes and wash.

2. *Chemicking.*—Steep the yarn for two hours under sieve in a solution of bleaching powder 2° Tw. (Sp. Gr. 1·01), then wash for half an hour under sieve.

3. *Souring.*—Steep the yarn for half an hour under sieve in dilute sulphuric acid 1° Tw. (Sp. Gr. 1·005), then wash for half an hour under sieve and afterwards through washing machine.

If the yarn is intended to remain white and not to be dyed, it is run through a so-called "dumping" machine with hot soap solution and blue (ultramarine, &c.), then hydro-extracted and dried.

When bleaching cotton thread, owing to its closer texture, the first three operations are repeated.

The boiling (also called "bowking" or "bucking") with caustic soda solution takes place in large iron boilers or "kiers." These are either open or provided with a lid capable of being screwed down, in order to be able to boil with a slight pressure of steam. The general appearance and internal arrangement of a low-pressure bleaching kier is well shown in Fig. 88.

The usual order of procedure is first to fill the kier with the yarn, and after blowing steam through for an hour or so, to run in the soda solution and boil for ten to twelve hours. The mode of circulation of the liquid through the goods is described on page 434.

The operations of chemicking, souring and washing under sieve, are carried out by means of the arrangement shown in Fig. 24. It consists of a stone tank E, with a false bottom F, and a valve G, communicating with the cistern D below; B is the shaft which works the pump C; F′ is a movable perforated drainer or sieve covering the whole surface of the tank E; A is a winch for drawing the chain of yarn into the tank. Supposing the tank to be packed with yarn, the pump is set in motion, the liquid in D is thus raised to the sieve F′, whence it showers down on the yarn below. It filters, more or less rapidly, through the yarn and collects again in the tank D to circulate as before.

Complete separate arrangements of this kind are required both for chemicking and for souring, but the washing under sieve is performed in either set of tanks as required, it being only necessary to stop the pump, close the valve G, and allow water to flow from a tap placed over the sieve, and to escape at the bottom of the tank E by a separate plug-hole into the nearest drain. The final washing after souring is best given by means of a machine similar to that represented in Fig. 62.

The "dumping" machine referred to is essentially the same in construction as the final washing machine,

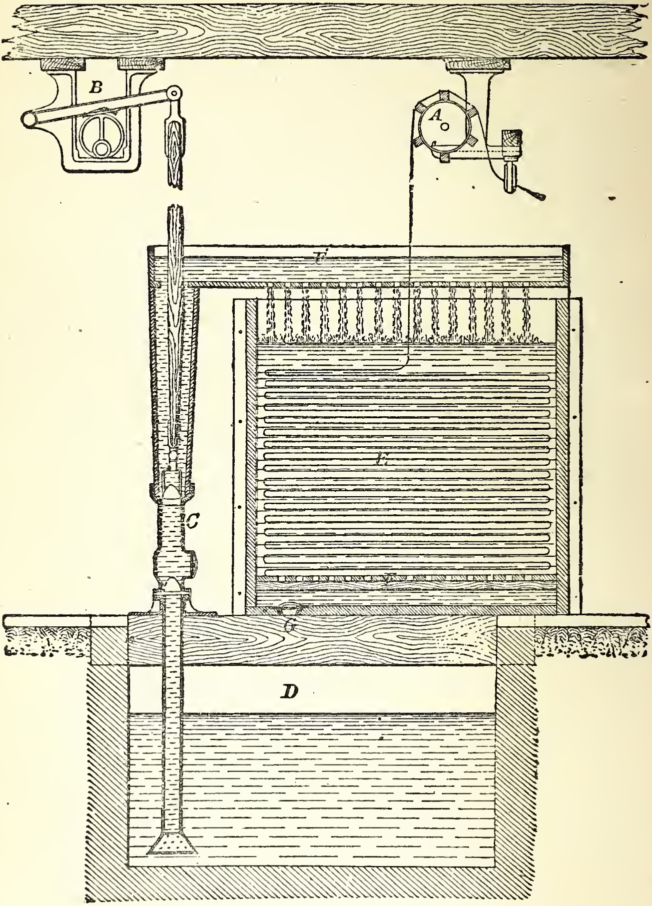


Fig. 24.—Apparatus for Chemicking, Souring, and Washing.

the main difference being that the square beater is replaced by a round roller, and that the upper squeezing roller is covered with cotton rope and rests loosely with its own weight on the lower one. As the cotton yarn, soaked with soap solution and blue, passes rapidly between the squeezing rollers, the irregularities produced by the plaiting or linking impart a constant jumping motion to the upper roller, and the liquid is effectually beaten and pressed into the heart of the yarn, thus enhancing considerably the purity of the white.

When the yarn is bleached as separate hanks and not in the chain, the washing is effected by one or other of the machines illustrated in Figs. 54, 55, 56, and the "dumping" is done in the "stocks" (*see* Fig. 52).

57. Bleaching of Cotton Cloth or Calico.—The mode of bleaching is varied according to the immediate object for which the bleached calico is intended; thus, one may distinguish between the *Madder-bleach*, the *Turkey-red-bleach*, and the *Market-bleach*.

MADDER-BLEACH.—This, the most thorough kind of calico-bleaching, was originally so-called because it was found specially requisite for those goods which had to be printed and subsequently dyed with madder. Its object is to effect the most complete removal possible of every impurity which can attract colouring matter in the dye-bath, so that the printed pattern may ultimately stand out in clear and bold relief on a white background of unstained purity. Although the madder-bleach is in general use among calico-printers, it may be also adopted by dyers whenever the calico is to be dyed subsequently in light and delicate colours, or if absolute freedom is desired from any impurity which resists the fixing of the colouring matter to be applied.

Stamping and Stitching.—For the purpose of subsequent recognition, the ends of each piece are marked with letters and figures, by stamping them with gas-tar or other substance capable of resisting the bleaching process. The pieces are then stitched together, end to end, by machinery.

Singeing.—This operation consists in burning off the nap or loose fibres which project from the surface of the cloth, since these interfere with the production of fine impressions during the printing process. It is performed by rapidly passing the cloth in the open width over red-hot plates or cylinders, or over a row of gas flames.

Fig. 25 shows a usual arrangement of the plate-singeing machine. By means of the rollers R, driven by a small engine, the piece G is rapidly drawn across the two red-hot copper plates P P, against which it is depressed by the four bars of the iron frame D, capable of being raised or lowered by the chain C. Immediately on leaving the plates, the piece passes between two perforated steam pipes K K, and through the water trough B, so that all adhering sparks may be at once extinguished; H is a hood for leading away the products of combustion. The two plates are heated by means of the furnace below.

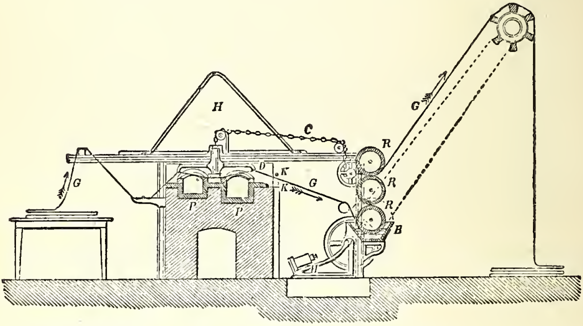


Fig. 25.—Plate-singeing Machine.

The great difficulty in plate-singeing is to keep the plates at a uniform strong red heat, owing to the rapid cooling action of the passing pieces; hence the "revolving singeing roller" is a decided improvement on the plate. In this arrangement the flames from the furnace pass through a copper cylinder which slowly revolves, so that a fresh red-hot surface is continually presented to the piece, and a regular even singe is thus obtained.

As a rule, hot-plate or cylinder singeing is preferred for thick heavy cloth, but for light, thin cloth—*e.g.*, muslins, &c.—singeing by gas is generally adopted.

The gas-singeing machine consists essentially of one or more rows of gas jets, across which the cloth is rapidly drawn. The gas is mixed with air just before being burnt, so that an extended line of the well-known smokeless Bunsen flame is presented across the full width of the piece; by means of levers the gas jets may be placed at any suitable distance from the cloth, or in case of accident they can be entirely withdrawn from it.

The preliminary work of stamping, stitching, and singeing is succeeded by the bleaching operations proper, which, for 24,000 kilos. cloth and with low pressure kiers, may be summarised as follows:—

1. Wash after singeing.
2. Lime-boil: 1,000 kilos. lime, boil 12 hours; wash.
3. Lime-sour: hydrochloric acid, 2° Tw. (Sp. Gr. 1·01); wash.
4. Ley-boils: 1st, 340 kilos. soda ash, boil 3 hours.
   2nd, 860 kilos. soda ash, 380 kilos. resin, 190 kilos. solid caustic soda, boil 12 hours.
   3rd, 380 kilos. soda ash, boil 3 hours; wash.
5. Chemicking: bleaching powder solution, $\frac{1}{4}$° — $\frac{1}{2}$° Tw. (Sp. Gr. 1·00125—1·0025) wash.
6. White-sour: hydrochloric acid, 2° Tw. (Sp. Gr. 1·01), pile 1—3 hours.
7. Wash, squeeze and dry.

1. *Wash after Singeing.*—The object of this operation is to wet out the cloth and make it more absorbent, also to remove some of the weaver's dressing. This was formerly effected by simply steeping the cloth in water for several days until, by the fermentation induced, the starchy matters were rendered more or less soluble. At present, printers' calicoes are not, as a rule, heavily sized, and a simple wash in the machine represented in Fig. 60 is sufficient. The pieces are drawn direct from the adjacent

singeing house, guided by means of white glazed earthenware rings ("pot-eyes"), through the washing machine; they are at once plaited or folded down on the floor and there allowed to lie "in pile" for some hours to soften. By this first operation, frequently called "grey-washing," the pieces, hitherto in the open width, assume the chain form, which they retain throughout the whole of the succeeding operations.

2. *Lime-boil* ("Lime-bowk").—The pieces are now run through milk of lime, a portion of which they absorb. They are at once drawn by overhead winches into the kiers and there plaited down and well packed by trampling under foot.

Fig. 26 shows the arrangement of a pair of Barlow's high-pressure kiers, one being given in section. The two kiers *a*, *b* are of strong boiler-plate iron; *g* is a false bottom, consisting of smooth water-worn stones, or a cast-iron grating, on which the cloth is laid; *d* is the distributor which acts also as a strengthening stay; the upper portion is perforated and closed by a stop at some distance from the bottom; the block *h* at the bottom of the distributor is perforated to allow liquor to pass from the kier; above, the distributor is connected with the two-way tap *t*, by which steam is admitted from the main pipe *m*, and by the reversing of which the steam is shut off and liquor admitted from the adjoining kier; *p p* is a pipe connecting the top of the kier *a* with the bottom of kier *b*, and *q q* similarly connects the top of kier *b* with the bottom of kier *a*; *s s* are branch steam pipes from the main *m*; *l l* are the pipes and taps through which the liquors are introduced into the kiers; *o o* are the manholes for entering and removing the cloth, and which can be made steam-tight by means of an iron plate held against the inner side with two crossbars and screw bolts; *w w* are the draw-off taps connected with the pipes *p* and *q*, and which can be worked from the stage at *c c* when emptying the kiers of spent liquor, &c.; *i i* are glass tubes or water-gauges which indicate when the liquor has passed entirely from one kier to the other; *u u* are short iron columns for supporting the kiers. The kiers are usually about three metres high and two metres in diameter.

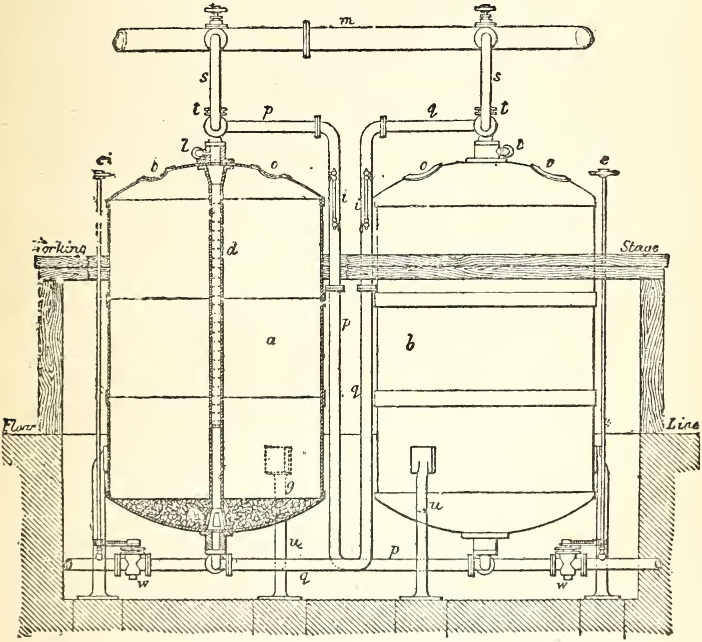


Fig. 26.—Barlow's High-pressure Kiers.

When the kiers are filled with cloth the manholes are closed, the pipes connecting the kiers are shut off, the emptying taps below are open, and steam is blown through for about a quarter of an hour to drive out the air, and to wet and heat the goods through. After running the necessary liquid into one of the kiers, the two-way taps are suitably arranged, high-pressure steam is again admitted, and the liquor is forced through the goods, out by the bottom, up the connecting pipe, and through the distributor into the goods contained in the other kier. When all the liquor has been transferred, both two-way taps are reversed, steam enters the second kier, and drives the liquor through the goods in the same manner back into the first kier. This alternating process is continued usually for about seven hours.

The essential action of boiling with lime is to decompose the fatty, resinous, and waxy impurities present in the fabric. They are not removed, but remain attached to the fibre as insoluble lime soaps, which can, however, be readily removed by the subsequent processes.

The colouring matter of the fibre is modified, and any alumina present is also attacked.

No doubt, caustic alkalis would also decompose and at once render soluble the fatty impurities, but lime is cheaper, and is said to attack the resinous matters more energetically. Care must always be taken that a sufficiency of water is present in the kier, otherwise the cloth, especially that at the top or the bottom, is liable to be tendered. Too much liquor is almost equally objectionable, since the pieces are then apt to become entangled and damaged by tremulous boiling.

3. *Lime-sour.*—This operation, also called the "grey sour," is immediately preceded by a washing of the pieces as they come out of the lime-boil. It consists in washing the pieces with dilute hydrochloric acid in a machine identical with that illustrated in Fig. 60. During this process the insoluble lime-soaps, resulting from the lime-boil, are decomposed and the lime is removed; any other metallic oxides present are also dissolved out, and the brown colouring matter is loosened. Hydrochloric acid is preferred to sulphuric acid because it forms a more soluble compound with the lime. Care must be taken to maintain the strength of the dilute acid as uniform as possible, both by having a regular

flow of fresh acid from a stock cistern, and by making occasionally rapid acidimetrical tests. After souring, it is advisable not to leave the pieces long in their acid state, for fear of the exposed portions becoming tender, but to wash them as soon as convenient. It is very essential, too, that this washing be as complete as possible, otherwise a tendering action may take place during the following process.

4. *Ley- or Lye-boil.*—The object of this operation is to remove the fatty matters still remaining on the cloth. The fatty matters having been decomposed during the lime-boil, and the lime having been removed from the lime-soaps by the souring, the fatty acids remaining on the cloth are readily dissolved off by boiling with alkaline solutions. The brown colouring matters are also chiefly removed at this stage. The boiling takes place in exactly the same kind of kiers as those used for the lime-boil. Other kiers besides Barlow's, however, are frequently used for both operations.

In the so-called "vacuum kiers," perfect penetration of the cloth by the liquors is obtained by first pumping out the air from the kier before admitting the liquors.

Fig. 27 gives the section of a modern "injector" kier A, filled with cloth; B B are the steam pipes, C is the injector, and D the circulating pipe; F is the liquor pipe, by which water or other liquid may be admitted; E E the draw-off valve and waste pipe. The kier being suitably filled with cloth and liquor, whenever the steam is turned on, the vacuum produced by its condensation in C withdraws the liquor from the kier and causes it to ascend the pipe D, to be at once showered over the pieces at G. A portion of the liquid may temporarily collect at H, but it soon percolates or is drawn through the cloth to the bottom, again to enter the injector. A continual circulation of the liquid is thus maintained.

If open or low-pressure kiers are used, similar to that referred to in cotton-yarn bleaching, the boiling is

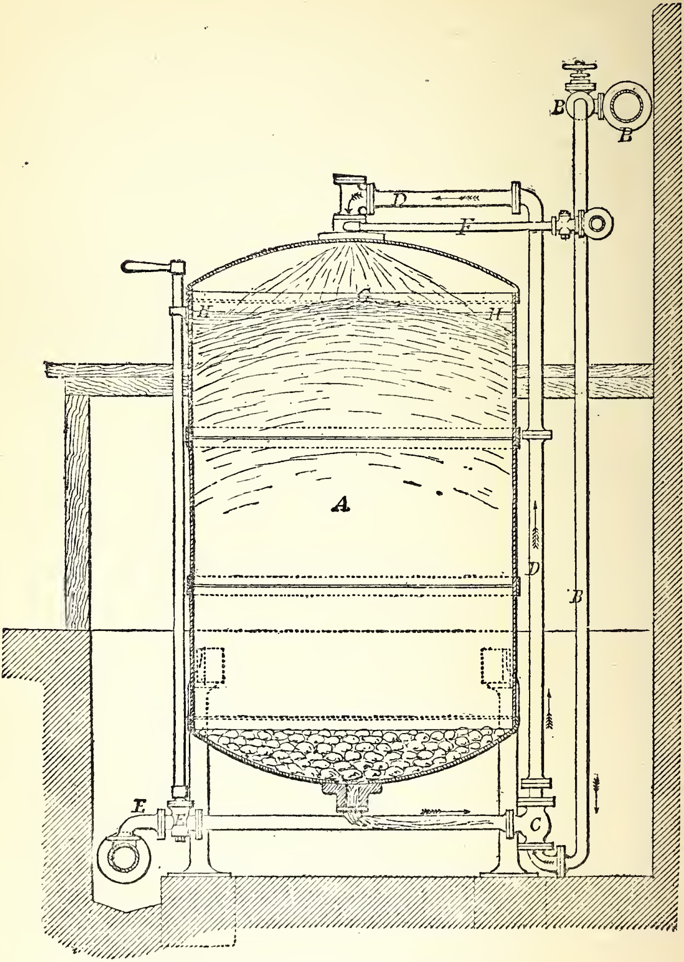


Fig. 27.—Section of Injector Kier.

continued for ten to twelve hours; with the injector kier and steam at fifty pounds pressure, three to four hours' boiling may be sufficient.

Some bleachers, as indicated on page 77, boil 1—3 hours with soda-ash alone, both before and after the resin boil, using 1—2 kilos. soda-ash per 100 kilos. calico. The first soda-ash boil, though not absolutely necessary, is advisable, in order to neutralise any traces of acid accidentally left in the cloth from the souring. Another plan to avoid tendering, is to let the goods steep in a weak soda-ash solution for a short time, and then to draw it off again before commencing the boiling operation with "resin-soap" This is termed "sweetening" the goods.

The boiling with resin-soap is a very special feature in the madder-bleach. Experiment has shown that resin-soap removes, better than any other substance which has been tried, certain matters, which would subsequently attract colouring matter in the dye-bath. What these particular substances are, and in what special manner resin-soap acts upon them, is at present unknown, or, at most, only conjectured.

The boiling with soda-ash solution after the "resin boil" is useful, in order to ensure the complete removal of fatty matters and undissolved resin.

Since the cloth is very liable to contract iron stains if left in the kier too long after the alkaline liquor has been drained away, it is well to wash immediately after the ley-boils.

5. *Chemicking.*—After all the previous operations the cloth still retains a faint yellowish or creamy tint, and the object of this operation is to destroy the traces of colouring matter from which it arises. The pieces are passed through a very dilute solution of chloride of lime or "bleaching-powder," in a "chemicking" machine, which is exactly similar to that employed for washing (Fig. 60), and are then allowed, while still moist, to remain in pile and exposed to the air

for a few hours or over-night. The bleaching action, which must be considered as one of oxidation, takes place largely during this exposure, hypochlorous acid being then liberated by the action of the carbonic acid of the air.

It is essential that the bleaching-powder solution should not be too strong, otherwise the cloth may be tendered or be partially changed into oxycellulose, and thereby be apt to attract certain colouring matters in the dye-bath, or to contract brown stains during subsequent steaming processes. For the same reason the solution of bleaching-powder should be entirely free from undissolved particles.

The bleaching power of the liquor should be maintained as constant as possible by having a continual flow of fresh bleaching-powder solution into the machine, and by occasionally testing how much of the liquor is required to decolorise a specially prepared standard solution of arsenate of soda, tinted with indigo extract or cochineal decoction.

6. *White-sour.*—This operation does not differ from the lime-sour already described. Its object is to complete the bleaching action by decomposing any "chloride of lime" still in the cloth, also to remove the lime, the oxidised colouring matter, and any traces of iron present. The cloth usually remains saturated with the acid a few hours.

7. The *final washing* must be as thorough as possible. It is usually performed by the square beater machine, illustrated in Fig. 62. The squeezing is done by the machine shown in Fig. 65. After squeezing, the cloth is again opened out to the full width, previous to drying. This is effected by allowing a lengthened portion of the chain of cloth to hang loosely and horizontally, and in this position to pass between a pair of rapidly revolving double-armed scutchers, which shake out the twists from the horizontal length of cloth. On leaving the scutchers, the piece passes in a state of tension over

one or more rollers provided with spiral projections, which tend to open out the cloth still more thoroughly; in this state it passes round the steam cylinders of the drying machine illustrated in Fig. 79.

The average length of time required for the madder-bleach is four to five days.

Turkey-red-bleach.—When calico is intended to be dyed Turkey-red it is not necessary to give it the madder-bleach, since no white ground has to be preserved. Certain modifications, too, are introduced; it is found, for example, that singeing, and the application of bleaching-powder which causes the formation of oxycellulose, interfere with the production of the most brilliant colour. The apparatus employed being similar to that already described, it is only necessary to give the following summary of the operations usually carried out:

1. Wash.
2. Boil in water for two hours and wash.
3. Ley-boils: 1st, 90 litres caustic soda, 70° Tw. (Sp. Gr. 1·35), boil ten hours and wash.
   2nd, 70 litres, ditto, ditto.
4. Sour: sulphuric acid, 2° Tw. (Sp. Gr. 1·01) steep two hours.
5. Wash well and dry.

The above quantities of materials are intended for 2,000 kilos. cloth, with low-pressure kier.

Market-bleach.—In market-bleaching the essential difference consists in the absence of the boiling with resin-soap, and the introduction of tinting the cloth with some blue colouring matter previous to drying. With many bleachers, the operation of chemicking comes between the two ley-boils, and not after them, as is usually the case.

Other bleaching agents than chloride of lime have been proposed for cotton, and even partially adopted—*e.g.*, hydrogen peroxide, permanganate of soda, &c.—but none have yet been able to supplant it, principally because of their greater cost. The same may be said regarding the mode of bleaching by means of the electrolysis of alkali chlorides

CHAPTER VI.

LINEN BLEACHING.

58. The bleaching of linen is more or less similar to that of cotton, although it is decidedly more tedious, owing to the larger proportion of natural impurities present in the flax fibre, and the greater difficulty of removing or decolorising them. These impurities consist principally of the brown insoluble pectic acid, which remains on the fibre after the retting process, to the extent of 25—30 per cent.

Linen is bleached in the form of yarn, thread, and cloth.

59. **Bleaching of Linen Yarn and Thread.**—Linen yarn is frequently only partially bleached, and one distinguishes yarns which are "half white" (cream), "three-quarters white," and "full white."

The following is an outline of the general method of bleaching linen yarn as at present adopted in Ireland. The percentages relate to the weight of yarn under treatment :—

1. Boil: 10 per cent. soda-ash, boil 3—4 hours; wash and squeeze.
2. Reel: bleaching powder solution, ½° Tw.; reel 1 hour; wash.
3. Sour: sulphuric acid, 1° Tw., steep 1 hour; wash.
4. Scald: 2—5 per cent. soda-ash, boil 1 hour; wash.
5. Reel: as No. 2; wash.
6. Sour: as No. 3; wash well and dry.

At this stage the yarn should be "half white."

If it is required "three-quarters white," the drying is omitted, and operations 4, 5, and 6, are repeated with the following slight modifications : (*a*) after the " scald " the yarn is "grassed," *i.e.*, spread on the grass in a field for about a week ; (*b*) instead of reeling the yarn in the solution of bleaching-powder, it is simply steeped in it for 10—12 hours, an operation which is analogous to the chemicking of cotton yarn (p. 72), and usually called the " dip."

If the yarns should be "full white" the same operations are again repeated once or twice, the duration of grassing being varied according to necessity and the weather. In each succeeding operation the concentration of the solutions employed is diminished.

The operation of boiling takes place in ordinary open or low-pressure kiers, while those of dipping, souring, and washing, are best performed in the apparatus illustrated in Fig. 24. In many establishments, however, the dipping and souring are effected by simply steeping the yarn in stone tanks filled with the necessary liquids, but owing to the absence of all circulation of the latter, this plan cannot be so effective. The washing is frequently done in wash-stocks, or dash-wheels, but this also is not good, because it tends to make the yarn rough.

The mode of applying the bleaching-powder solution in the earlier stages by " reeling," is peculiar to linen yarn bleaching. Its primary object has probably been to ensure regularity of bleach, but since the carbonic acid of the air decomposes the calcium hypochlorite more readily by this means, and liberates hypochlorous acid within the fibre, as it were, the bleaching must be more thorough and greatly accelerated.

The reeling machine consists of a large shallow stone cistern holding the solution of bleaching-powder, and provided with a movable framework supporting a number of reels. On these are suspended the hanks of yarn in such a manner that only their lower ends dip into the liquid. Each single reel can be readily detached if necessary, or, by means of a hydraulic lift, the whole framework with reels and yarn can be raised and withdrawn from the liquid, and at once transferred to another and similar cistern for the purpose of washing, &c. Some bleachers use this machine for scalding.

It is said that better results are obtained if the calcium hypochlorite is replaced by the corresponding magnesium compound. Probably the best agent to use would be sodium hypochlorite, since there would then be no formation on the fibre of any insoluble carbonate, and washing might largely replace the souring, in which case weaker acids even than those mentioned could be used. Since calcium chloride is more soluble than the sulphate, it seems likely that where calcium hypochlorite is used, hydrochloric acid would be better as a souring agent than sulphuric acid.

60. Bleaching of Linen Cloth.—The following is an outline of a modern Irish process for 1,500 kilos. brown linen (lawns, handkerchiefs, &c.), with low-pressure kiers:

1. Lime-boil: 125 kilos. lime, boil 14 hours; wash 40 minutes in stocks.
2. Sour: hydrochloric acid, 2½° Tw. (Sp. Gr. 1·0125), steep 2—6 hours; wash 40 minutes in stocks; "turn hank," and wash 30 minutes in stocks.
3. Ley-boils: 1st, 30 kilos. caustic soda (solid), 30 kilos. resin, previously boiled and dissolved together in water; 2,000 litres water; boil 8—10 hours; run off liquor, and add—
   2nd., 15 kilos. caustic soda (solid), dissolved; 2,000 litres water, boil 6—7 hours; wash 40 minutes in stocks.
4. Expose in field 2—7 days, according to the weather.
5. Chemick: chloride of lime solution, ½° Tw. (Sp. Gr. 0·0025), steep 4—6 hours; wash 40 minutes in stocks.
6. Sour: sulphuric acid, 1° Tw. (Sp. Gr. 0·005), steep 2—3 hours; wash 40 minutes in stocks.
7. Scald: 8—13 kilos. caustic soda (solid) dissolved, 2,000 litres water, boil 4—5 hours; wash 40 minutes in stocks.
8. Expose in field, 2—4 days.
9. Chemick: chloride of lime solution, ¼° Tw. (Sp. Gr. 0·00125), steep 3—5 hours; wash 40 minutes in stocks.

The goods are examined at this stage; those which are sufficiently white are soured and washed, and those which are not are further treated as follows:—

10. Rub with rubbing boards and a strong solution of soft soap.
11. Expose in field 2—4 days.
12. Chemick: chloride of lime solution, $\frac{1}{8}$° Tw. (Sp. Gr. 0·0006), steep 2—4 hours; wash 40 minutes in stocks.
13. Sour: sulphuric acid, 1° Tw. (Sp. Gr. 0·005), steep 2—3 hours; wash 40 minutes in stocks.

When the cloth (cream linen) is made of yarn already partially bleached, a less severe process is required, *e.g.*, less lime is used in the lime-boil; only one ley-boil is given, and that with resin-soap instead of caustic soda; weaker chloride of lime solutions are used; the scald is effected with soda-ash solution; and operations 8 and 9 are omitted.

What is known as "brown holland" is a plain linen cloth which has had little or no bleaching, but only a short boiling in water, or in weak soda-ash solution, followed by a weak souring. It possesses, therefore, more or less the natural colour of the retted flax fibre.

The washing is usually effected in the wash-stocks (Fig. 52), but sometimes, and with advantage too, in so-called slack-washing machines. These are similar in construction to that represented in Fig. 60; the washing trough, however, is divided by wooden spars into several compartments, each capable of holding several yards of slack cloth between each nip.

The "rubbing" referred to is a characteristic feature in linen cloth bleaching, and has for its object the removal of small particles of brown matter called "sprits." It is effected by a special machine which consists essentially of a pair of heavy corrugated boards resting on each other; the upper one is moved lengthwise to and fro, while the pieces are led laterally between them.

The exposing of the goods in a field to the influences of air, moisture, and light, or "grassing," as it is technically termed, is still very generally adopted in order to avoid steeping too frequently in solutions of bleaching-powder, and thus to preserve as much as possible the strength of the fibre.

"Turn-hanking" consists in loosening the entangled pieces and refolding them, so that every part may be exposed to the action of the hammers of the wash stocks; the operation is introduced as often as required at various stages of the bleaching process, but especially after washing in the stocks.

61. Chemistry of Linen Bleaching.—During the several boilings with lime, soda-ash, caustic soda or resin-soap, the insoluble brown-coloured pectic acid of the retted fibre is decomposed, and changed into metapectic acid, which combines with the alkali to form a soluble compound. According to the origin of the flax, the loss which it thus sustains may vary from 15 to 36 per cent.

By the application of bleaching-powder alone, the brown pectic matters are bleached only with great difficulty, and even then only by using "chloride of lime" solutions of such concentration that the fibre itself is apt to be attacked. After a number of successive boilings with alkali, however, the goods retain merely a pale grey colour, which is readily bleached by comparatively weak solutions without injury to the fibre.

The rational mode of bleaching linen would seem to be, therefore, to defer the application of the bleaching-powder until the pectic matters have been almost or entirely removed by lime and alkaline boilings, although, in practice, this plan is never strictly adhered to. A single ley-boil scarcely removes more than 10 per cent. of the pectic matters, and since their presence in such large proportion prevents the solutions of bleaching-powder from decolorising the whole of the grey matter at one operation, the usual plan is to alternate the alkaline boilings with dilute chloride of lime treatments; the more so because it is considered that a slight oxidation of the pectic matters facilitates their removal by the alkaline boilings, and that the latter predispose them to oxidation.

Well-bleached linen ought not to be discoloured when steeped in a dilute solution of ammonia; if by this treatment the linen acquires a yellow tint, it is a sign that the pectic matters have not been entirely removed.

The usual period required for bleaching brown linen varies from three to six weeks.

CHAPTER VII.

WOOL SCOURING AND BLEACHING.

62. **Object of Scouring Wool.**—The "scouring" of wool has for its object the complete removal of all those natural and artificial impurities (yolk, dirt, oil, &c.) which would otherwise act injuriously during the processes of weaving or dyeing.

The paramount importance of having woollen material thoroughly well cleansed or scoured previous to dyeing, cannot be too much insisted upon. If the operation be omitted, or be improperly or incompletely performed, each fibre remains varnished, as it were, with a thin layer of fatty matter, which resists to a greater or less degree the absorption and fixing of mordant or colouring matter. The final result is, that the material is badly or unevenly dyed, and appears "flecked," "stripey," &c., or since the colouring matter can only be superficially deposited, it is readily removed by the subsequent operations of washing, milling, &c.

It has already been mentioned, when considering the wool fibre, that *raw-wool* is impregnated or encrusted with yolk, consisting essentially of certain fatty matters, free fatty acids, &c. Woollen *yarn* and *cloth* always contain oil (olive oil, oleïc acid, &c.) to the extent of about 10—15 per cent., which has been sprinkled on the wool for the purpose of facilitating the spinning process.

It would be a great advantage, however, if manufacturers would begin to use neutralised sulphated castor-oil or castor-oil soap solutions instead of oil, for this purpose. Cloth which required milling after dyeing (*e.g.*, mixtures, tweeds, &c.), or previous to dyeing, would then need no scouring with alkali, but merely a simple washing in soft water. This plan is already adopted with success in Belgium.

The method of removing yolk, oil, &c., from wool, which first suggests itself, is that of saponifying or emulsifying them by means of weak alkaline solutions, and such, indeed, are the agents most largely employed for the purpose of wool scouring.

The choice of the most suitable alkaline scouring agent and the best temperature to be employed depend upon the quality and origin of the wool.

In modern times other agents of a volatile nature, and capable of dissolving fatty substances, have been proposed and to some extent employed—*e.g.*, fusel oil, ether, light petroleum oil, carbon disulphide, &c.—and it is by no means improbable that some member of this class will form the wool-cleansing agent of the future. It must be remembered, however, that these volatile liquids are essentially solvents for fatty matters, and not for alkaline oleates. A washing in water would therefore always have to take place in addition.

63. Scouring Agents.—*Lant* or *stale urine* is the detergent which has been employed for wool-scouring from the earliest times, and it is effective because of the ammonium carbonate it contains. Though still used, this agent has been largely supplanted by others, such as ammonia, sodium carbonate, soap, &c.

Stale urine, used in the proportion of one measure to about five of water, gives excellent results in most cases. It leaves the wool clean and with its normal physical properties of softness, elasticity, &c., unimpaired, its disagreeable odour being its main defect. *Ammonium carbonate* is the most rational substitute for "lant," and represents, perhaps, one of the best alkaline detergents, especially if used along with soap; but it is still too expensive for general use. As a mild scouring agent for the better classes of wool, *potash or soda soap* is largely employed. Satisfactory results are obtained with these if the soap is of good quality, and free from excess of caustic or carbonated alkali. Other things being equal, the most soluble soaps are to be preferred, such as potash soaps, or soda soaps made from oleïc acid. An average soap solution may contain 30—50 grams of soap per litre of water. An addition of ammonia to the soap solution is frequently made for the purpose of increasing its detergent properties. An important consideration to be remembered when using soap is, that the water should be as free as possible from lime and magnesia (*see* p. 123) to avoid the formation of lime and magnesia soaps.

The scouring agent most largely employed, either alone or mixed with soap, is *sodium carbonate*, of which excellent qualities (Solvay soda, "Crystal carbonate," &c.) are now to be had. When used with judgment and care, it leaves the wool but little affected, and being inexpensive it is well adapted for wools of medium and low quality. The injurious effects of using a calcareous or magnesian water are less marked with this agent than with soap, since the calcium and magnesium carbonates precipitated on the wool are of powdery nature and more readily removed. The presence of caustic soda must always be rigidly avoided. The concentration of the soda solution should be such that it stands at 1°—2° Tw. (Sp. Gr. 1·005—1·01), or say 10—20 grams $Na_2CO_3.10H_2O$ per litre. It may be stated, as a general rule, that the best results are obtained (*i.e.*, as regards feel and lustre of wool) by using the solutions of alkaline detergent as dilute, and at as low a temperature, as is consistent with the complete removal of all impurities. The temperature may vary from 40° to 55° C.

Other substances have from time to time been recommended as useful additions to the scouring bath, *e.g.*, common salt, ammonium chloride, decoction of soap bark (*Quillaya saponaria*), oleïn, resin soap, pigs' manure (Seek), &c. Some of these may act beneficially in certain cases, but as a rule the previously mentioned scouring agents are more generally useful. Ammonium chloride may de-alkalise soap, or if used along with sodium carbonate may be beneficial because of the ammonium carbonate produced. Oleïn and resin-soap probably assist emulsification, while *seek*, which is frequently employed, is effective because of its alkalinity.

Patent or secret scouring substitutes should be strictly avoided; they are either worthless, or, if useful, they can be prepared by the scourer himself more economically. Secrets both in scouring and in dyeing belong rather to the past than to the present age.

64. Loose-Wool Scouring.

a. Scouring with Alkaline Solutions.—In its most complete form the scouring (Fr., *lavage*) of raw or greasy wool should consist of at least three operations:—

1st. *Steeping* or *washing* with water (Fr., *désuintage*).

2nd. *Cleansing* or *scouring proper* with weak alkaline solutions (Fr., *dégraissage*).

3rd. *Rinsing* or *final washing* with water (Fr., *rinçage*).

In England the first operation is omitted, sometimes because the wool has been already more or less completely washed by the wool grower, in order to lessen the expense of transport, but more frequently because the opinion prevails that the operation is unnecessary and only entails additional expense. It is contended, and indeed with some degree of truth, that the soluble portion of the yolk, owing to its alkaline nature, renders material assistance in the scouring bath.

On the other hand, this system has certain defects. The scouring bath becomes more readily soiled and rapidly varies in composition, so that, unless it be frequently renewed, it soon scours the wool insufficiently, or may even stain it injuriously. Under ordinary circumstances, and scouring with sodium carbonate or with soda soaps, the yolk is entirely lost.

When the wool contains only a small percentage of yolk, the steeping process for the recovery of yolk-ash may well be omitted, but its adoption in the case of wools rich in yolk (*e.g.*, Buenos Ayres wool, &c.) is certainly to be recommended as distinctly advantageous. In Belgium and France it is largely carried on.

Steeping.—To be effective the process must be systematic, the water should be heated to about 45° C., and the wool if possible agitated.

In practice, the last point **is** not attempted on economical grounds, and the wool is simply steeped in, or rather systematically washed with, tepid water in the following manner :—

Four or five large iron tanks capable of being heated by steam are filled with the raw wool. The first one is then filled with tepid water (45° C.) and the wool is allowed to steep for several hours until, indeed, no further quantity of yolk is dissolved ; by means of a siphon, steam-injector, pump, or other means, the liquid is removed to the second tank, where it is also allowed to remain (at 45° C.) until it again ceases to dissolve yolk ; it is then in like manner removed to tanks 3 and 4, until finally it becomes perfectly saturated with yolk, and is ready for being evaporated to dryness, calcined, &c., to obtain the yolk-ash. Simultaneously with what has just been described, *fresh* water (45° C.) is made to circulate in a similar manner through the several tanks, until at length the wool in tank No. 1 is entirely deprived of the soluble constituents of the yolk ; the wool being now ready for the scouring. This tank is emptied and refilled with raw wool. So soon as this has taken place, the steeping water is made to circulate through the tanks in the order of Nos. 2, 3, 4, 1, so that the saturated yolk solution is now drawn off from the newly filled No. 1 tank, and the wool contained in No. 2 tank is exhausted, which is then duly emptied and refilled. By this method the wool in each tank becomes, in turn, gradually deprived of yolk, and supposing the tanks to be arranged in a circle, the points at which the fresh water is introduced and the saturated yolk solution withdrawn, are always two contiguous tanks, and move gradually round the circle. The main principle of the process is, that the raw greasy wool is always first washed with water already pretty well saturated with yolk, the partly extracted wool is brought into contact with weaker yolk solutions, while the most thoroughly exhausted wool is washed with fresh water.

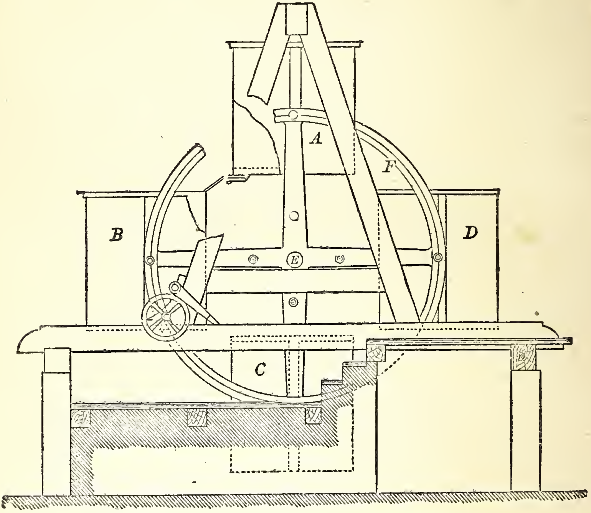


Fig. 28.—Wool-Steeping Tanks.

Figs. 28 and 29 represent an arrangement of washing tanks designed by H. Fischer with a view to economise space and labour.

A, B, C, D, represent four iron tanks suspended between two large wheels F, having the common axis E. One of the wheels is provided with teeth, which work against the small cog-wheel of a windlass, the arrangement being such that the whole apparatus can be readily turned at G by a single workman. Each tank can thus be raised in turn to a high level for the purpose of draining the wool it contains and running the liquid into the next tank.

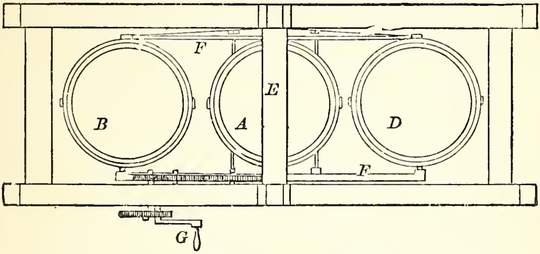


Fig. 29.—Wool-steeping Tanks.

The following numbers giving the amount of dry yolk in yolk solutions of different degrees of concentration are calculated from data published by Havrez :—

Spec. Gravity of yolk solution.	Degrees Twaddell.	Amount of dry yolk contained in one litre.
1·377	75·4	769 grams.
1·215	43	376 ,,
1·102	20·4	175 ,,
1·048	9·6	72 ,,
1·025	5	37 ,,
1·012	2·4	17 ,,
1·006	1·2	8 ,,

According to M. Chandelon, 1,000 kilos. of raw wool may furnish 313 litres of yolk solution of Spec. Grav. 1·25 (50° Tw.), having a value of 15s. 6d., while the cost of extraction does not exceed 2s. 6d.

Fig. 30 represents a furnace for the manufacture of carbonate of potash from yolk, devised by H. Fischer.

The concentrated yolk solution is first put into the tank *a* and warmed by the waste heat of the furnace. Sometimes tank *a* is situated at a high level and the concentrated yolk solution is led into the chimney, where it trickles down in a zig-zag course across overlapping steps at once into the chamber *b*. The flow can be so regulated that the level of the liquid in *b* is constant. In the regular course of work the liquid is run from the tank *a* into the evaporating chamber *b*, and when partly evaporated here, it is led by a connecting pipe into the calcining chamber *c*, where it is evaporated down to a thick syrupy consistency. Very soon, owing to the organic matter contained in it, it ignites, and the fire at *d* can be much moderated. The calcined mass in *c* is worked about with a rake until it acquires a dirty grey colour, when it is withdrawn and allowed to cool. In the meantime, the liquid in *b* has been evaporating, and fresh liquid has been warmed in *a*. When properly managed the process is almost continuous. Care must be taken in admitting new liquid from *b* into the red-hot chamber *c*, since it froths up very considerably. The pipe connecting *b* and *c* is so arranged that it can be readily removed and cleaned. Comparatively little coal is required, since it is largely economised through the burning of the organic matter of the yolk itself. It has been found in

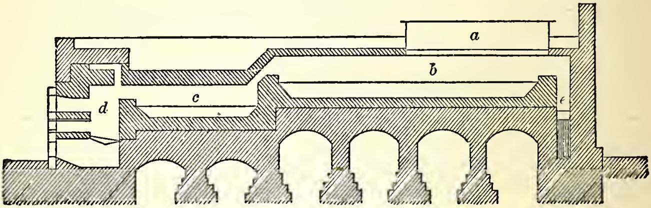


Fig 30.—Section of Furnace for Making Yolk-ash.

practice, that to evaporate 12 kilos. of water in such a furnace 1 kilo. of coal is required. Yolk-ash is recovered in Roubaix, Antwerp, Verviers, Louvain, Brugge, Hanover, Döhren, and Bremen.

Scouring and Washing. — In small establishments the wool is thrown (and, indeed, without previous steeping) into a large tank filled with the scouring liquid, and worked about by hand for a short time with poles. It is then lifted out with a fork, drained on a wooden screen, and well washed several times in a cistern having a perforated false bottom. When soap is used, the excess of liquid is removed by a pair of squeezing rollers before washing. Obviously, by this method the wool is only incompletely or irregularly scoured, hence in large and well-equipped establishments, after "steeping," it is passed through the wool-scouring machine. There are many varieties, *e.g.*, those of Petrie, M'Naught, Crabtree, Sirtaine and Melen, &c., but it is beyond the province of this work to discuss their different points of merit. As a typical representative, the rake-machine (Fig. 31) of M'Naught may be described.

It consists of a large cast-iron trough, provided with an ingenious arrangement of forks or rakes. The wool is introduced at one end of the trough and evenly spread on an endless apron or feeder situated at *a*. It is immediately pressed beneath the surface of the scouring solution by the rotating immerser *b*, and then gradually passed forward by the to-and-fro digging motion of the reciprocating rakes *c*, *c'*. At *e* there is suspended a stationary oblique rake or grating, which the reciprocating rakes intersect; its purpose is to prevent a too rapid forward progression of the wool. By the movement of the rakes, the wool is well worked in the scouring liquid and carried gradually to the other end of the trough. It is there lifted out by a swing rake *c'* and the special mechanism *f*, then passed through a pair of squeezing rollers and thrown off by a fan *g* in a loose, open condition. The wool is afterwards washed

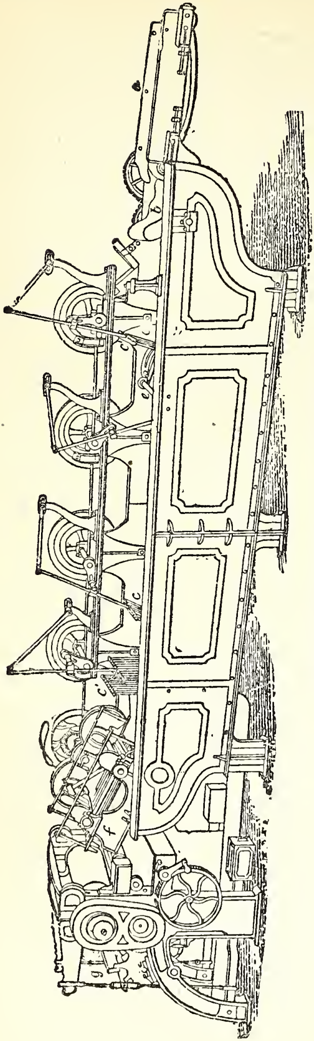


Fig. 31.—Rake Wool-scouring Machine.

with water in a similar machine.

A really effective scouring arrangement consists of at least three such machines, placed in line, so that the wool may be passed automatically from one to the other. The operation of scouring and washing thus becomes continuous, regular, and complete.

The first machine into which the wool is introduced contains more or less soiled scouring liquor, which has already been used in the second trough; the latter contains fresh scouring liquor, and the third a continual flow of clean, cold, or preferably tepid, water. Each trough is fitted with a perforated false bottom, beneath which dirt may collect, and each pair of machines is connected with an injector pipe, for the purpose of transferring the liquor from one to the other, as occasion requires, in a direction opposed to that of the movement of the wool.

The great object of the wool-scourer should be, to maintain the composition of the second bath as constant as possible, or at least not to allow it to become too much soiled. This is effected partly by the squeezing rollers between the first and second machines, and partly by emptying the first bath the moment it gets charged with fatty matter, transferring to it the slightly-soiled liquor of the second bath, and refilling the latter with fresh scouring solution. No doubt a still more regular and complete scour would be obtained by having a range of four troughs instead of three. If the amount of fatty matter remaining in the wool after scouring exceeds 1 per cent., the operation must be regarded as having been inefficiently performed.

Magma Process.—The waste scouring liquor ought to be collected in stone lined pits, and there neutralised or acidified with sulphuric acid. The magma of fatty matter which rises to the surface is collected, drained in filter bags, and sold to oil dealers. If soap has been the scouring agent employed, the fatty acids thus recovered are all the more valuable, but in any case the spent scouring liquors should never be allowed to pollute the neighbouring stream.

b. Scouring with Volatile Liquids.—This is more advantageous than the alkaline method, because it deprives the wool more completely of its wool-fat, and the injurious effect of the alkalis is entirely removed. On the other hand, the method is more costly, and by the use of *some* extracting liquids the wool may certainly be modified.

Some consider that since oil must be added to the wool before spinning, it is not necessary to remove the whole of the natural fatty matters from raw wool. Whether this view be correct or not as far as spinning is concerned, it is certainly not to be entertained if the loose wool has to be dyed

Up to the present time, wool scouring with volatile liquids has not met with general acceptance, partly because of the attendant danger if not employed with great care and with suitable appliances. The difficulties, however, are not insuperable, and have, indeed, been more or less overcome by Da Heyl, Van Haecht, and others.

One method recently proposed is that of T. J. Mullings. The wool is placed in an enclosed centrifugal machine, and submitted to the action of disulphide of carbon. When this liquid is saturated with yolk, the machine is set in motion to remove the bulk of it, the remaining portion being expelled by admission of water. The wool is afterwards washed with water in the usual washing machines. The novel feature in the process is the expulsion of the carbon disulphide by displacing it with water, by which means the wool does not acquire the yellow tint it invariably assumes when heat is employed for this purpose. The mixture of carbon disulphide and water is collected in a tank; after settling, the former is drawn off from below and recovered for subsequent use by distillation. Experiments are said to have shown that wool cleansed in this way is stronger, and will spin finer yarn, and with less waste, than if scoured by the ordinary method with soap, and this is done at one-eighth of the usual cost. This process has been recently tried on a large scale with a certain degree of success.

65. **Yarn Scouring.**—The scouring of woollen yarn is more readily effected than that of raw wool if the oil with which it has been impregnated by the spinner has been of good quality (*e.g.*, olive oil). It has always been considered that the difficulty is increased if cheap oils have been used which contained an appreciable amount of mineral oil, since this, being a hydro-carbon and not a glyceride, is unsaponifiable. Experiments by C. Roth seem to show, however, that this view is erroneous.

a. Stretching of Yarn.—Those yarns which are hard twisted require this preliminary process in order to remove their curly appearance and to prevent them from shrinking during the subsequent scouring operation.

For this purpose the "yarn-stretching" machine (Fig. 32) is employed.

It consists of two vertical iron screws D, connecting

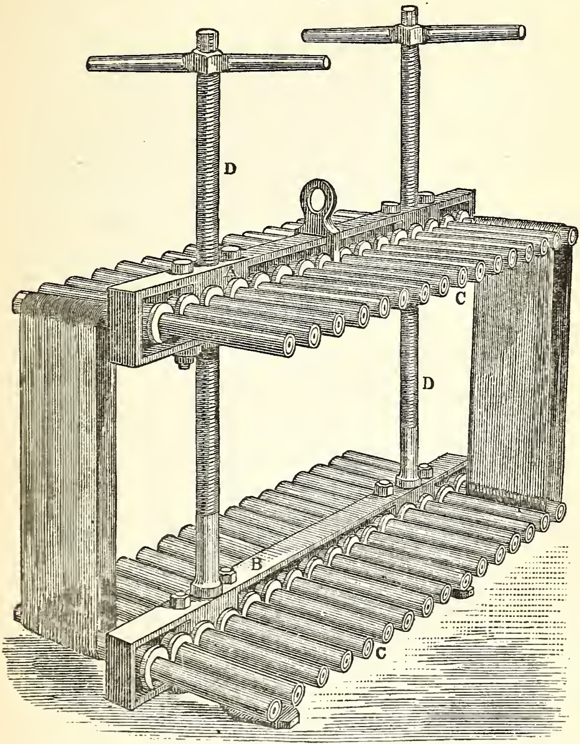


Fig. 32.—Yarn-stretching Machine.

two horizontal bars A, B, one above the other, each fitted with a series of metal pegs or arms C, on which the hanks are suspended. The lower bar B is fixed, while the upper one A is capable of being moved up

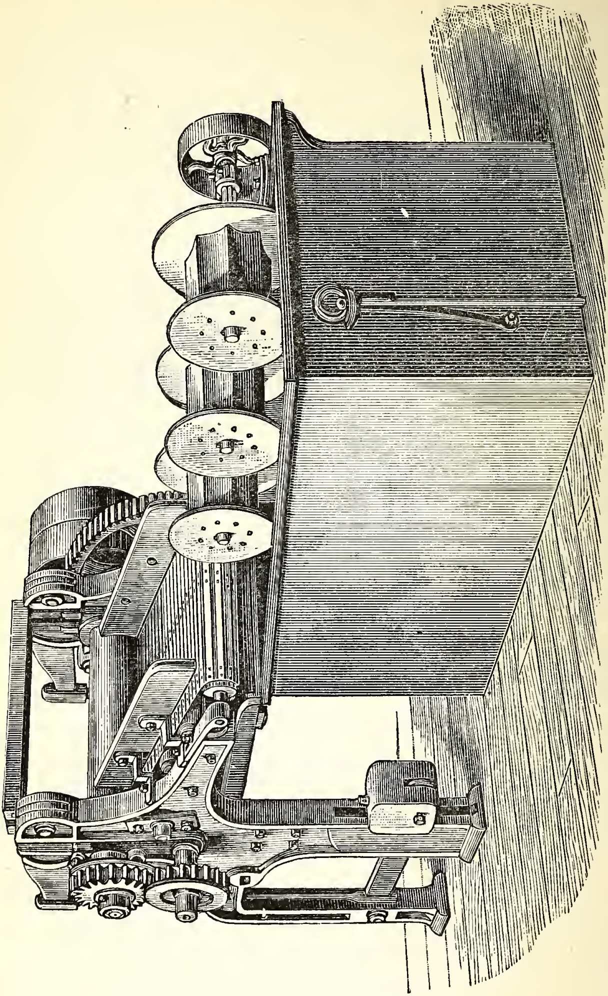


Fig. 33.—Woollen Yarn-scouring Machine.

or down by turning the vertical iron screws, and fixed at any point. After filling the arms C with yarn, as indicated in the figure, the bar A is screwed up until the yarn is suitably stretched. In this condition the whole apparatus is immersed in a bath of boiling water, and after a few minutes removed. Those portions of the hanks immediately in contact with the pegs are still unaffected and look curly. Hence after relaxing the tension of the hanks, their positions on the pegs are changed, they are again screwed up, and the immersion in boiling water is repeated. When taken out and allowed to cool, the yarn is taken off ready for scouring.

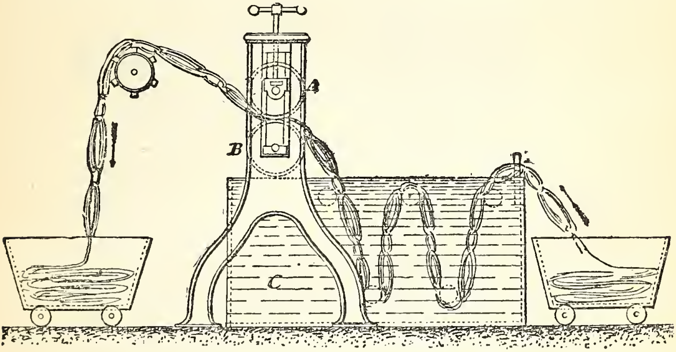


Fig. 34.—Continuous Woollen Yarn-scouring Machine.

The principle of the operation has been referred to in speaking of the hygroscopic and elastic nature of the wool fibre (*see* p. 28).

b. Scouring of Yarn.—Yarn scouring is generally done by hand in an ordinary rectangular wooden tank, the liquor being heated by means of a perforated copper steam-pipe. The hanks are suspended on smooth wooden rods placed across the tank, on each side of which stands a workman (*see* Figs. 45, 70). One by one the rods full of yarn are taken up, once or twice swayed to and fro, and then each hank is carefully lifted up and turned, so that the exposed portion resting on the rod may become immersed. This is frequently facilitated by means of a second and thinner rod, which is inserted in the loop of the hanks, immediately beneath the suspending rod, so that the whole rod full of hanks may be turned at once, and without scalding the hands. The whole operation is systematically repeated during fifteen to twenty minutes, after which the yarn is transferred to a second tank containing cleaner scouring liquid. Here the process of turning is repeated, after which the yarn is washed, either by the same method or by placing the rods full of hanks on a pair of horizontal bars, situated beneath a perforated wooden tray, on which water is flowing ; the yarn thus receives an efficient shower bath.

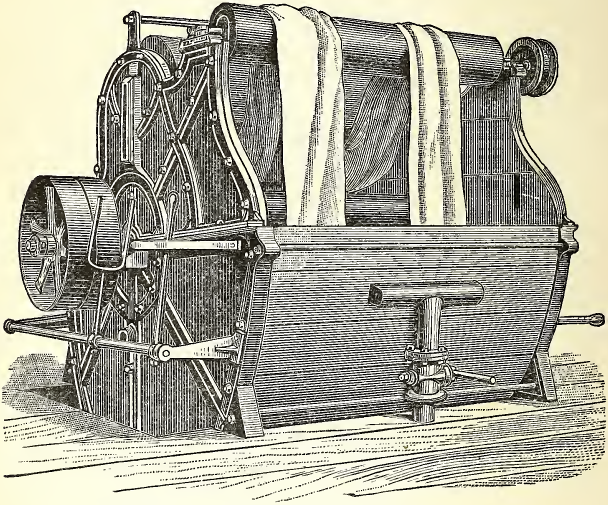


Fig. 35.—Woollen Cloth-scouring Machine.

Scouring partly by hand and partly by machine is effected by the apparatus represented in Fig. 33, and made by Thos. Aimers and Sons, Galashiels.

The yarn is suspended on reels projecting from one side of the scouring box, and caused by steam-power to revolve in the scouring solution alternately in each direction for a short time. The hanks are then taken off the reels, placed on a moving endless band, and thus led through a pair of squeezing rollers, to be washed with water in a similar machine. In some machines the reels are omitted, and the hanks worked in the liquid by hand.

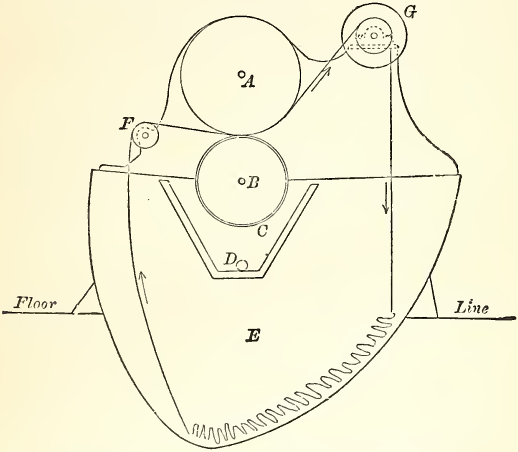


Fig. 36.—Section of Machine shown in Fig. 35.

A perfectly continuous method of scouring by machinery alone, is that in which the loose hanks of yarn are placed on a feeding apron, and borne along between two broad endless bands, through a succession of scouring baths fitted with a series of squeezing rollers.

Another continuous method is that carried out by means of the machine represented in Fig. 34.

The hanks are linked together by means of a small knotted and twisted loop of cord. The chain of yarn thus formed is then passed continuously through a series of three machines, similar to the one represented, C. The squeezing rollers A and B are thickly covered with some soft, durable material, *e.g.*, silk noils.

66. Cloth Scouring.—Woollen cloth is either scoured in the "chain" form or in the open width, the latter being the preferable mode, since the operation cannot but be thus more evenly performed, and does not tend to produce creases in the material.

Figs. 35 and 36 represent (in perspective and in section) the common chain-scouring machine, usually termed a "dolly." It consists essentially of a pair of heavy wooden squeezing rollers A B, placed over a box or trough C containing the scouring solution. The pieces are stitched end to end, to form an endless band, and this is made to pass continuously for twenty minutes or so between the rollers, the lower one of which, since it is partially immersed, carries the solution to the cloth. D is a steam pipe for heating the scouring solution, E an empty wooden box, F and G are guiding rollers. The operation is repeated with fresh solution in another similar machine, and the pieces are afterwards washed with clean water.

The machine employed for scouring cloth in the open width is shown in Fig. 37. It is much broader than the one just described, in order to suit the width of the cloth, and certain straining bars F are required for the purpose of keeping the cloth opened out and free from creases previous to its passage between the squeezing rollers A, B, which are preferably of iron, in order to give a more equal pressure across the whole width of the cloth. Immediately below these rollers is the trough C containing the scouring solution. The perforated water-pipe H is used when the pieces are washed in this machine after scouring.

67. Scouring of Union Goods.—The scouring of thin materials with cotton warp and woollen weft presents certain difficulties. The different hygroscopic, elastic, and other physical properties of cotton and wool, cause such materials, if simply scoured in the ordinary way, to contract or shrink irregularly over the whole surface of the fabric, so that they assume, when dried, a rough

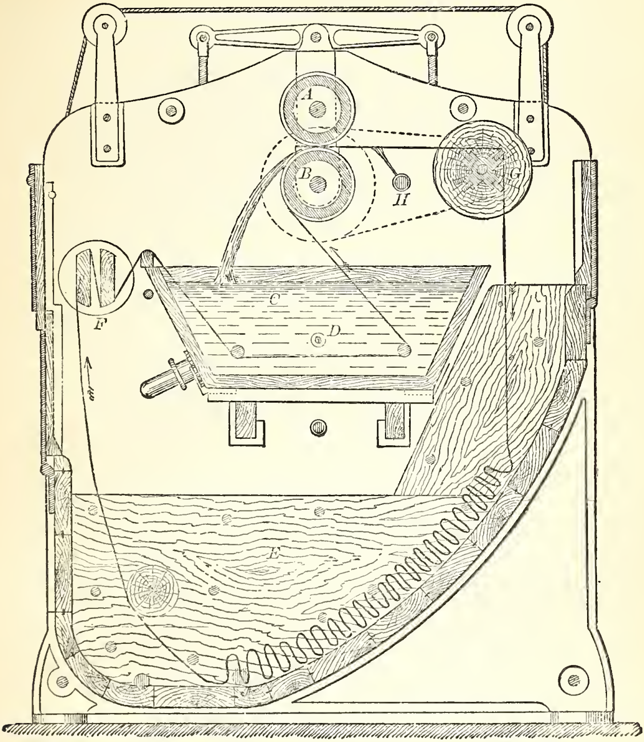


Fig. 37.—Woollen Cloth open-width Scouring Machine.

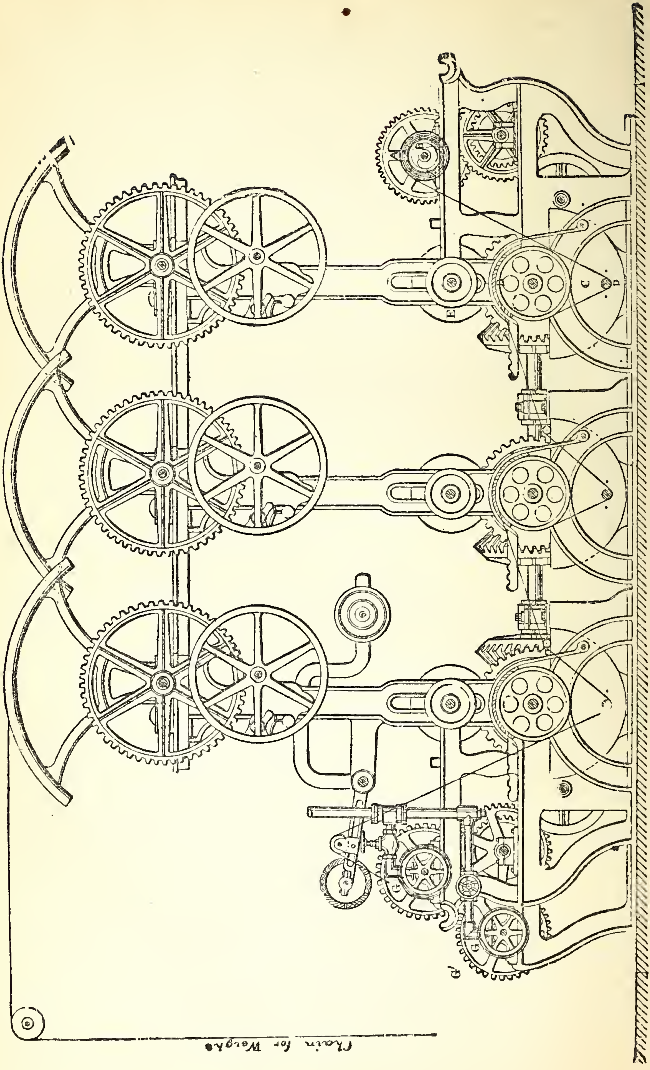


Fig. 38.—Treble Crabbing Machine.

shrivelled appearance which renders them quite unsaleable. Special appliances and methods are in consequence required. The scouring of thin union goods comprises the operations of *Crabbing*, *Steaming*, and *Scouring*.

(*a*) *Crabbing or Fixing.*—The object of this and the following operation is to prevent the material from acquiring the "cockled," "curled," or shrivelled appearance above alluded to. It also imparts a permanent and indestructible lustre and finish of a peculiar quality, which is not removed or affected by any subsequent operation.

Fig. 38 shows the arrangement of a treble crabbing machine.

The cloth A wrapped on the roller or beam B is passed in the open width, and in a state of tension, below the roller D and through boiling water contained in the vessel C, then immediately between the pair of heavy iron rollers B and E, under great pressure. It is at once tightly wrapped or beamed on the lower roller B, therefore, while still revolving in the hot water. The process is repeated with boiling water in the second trough, and again with cold water in the third trough. The tension of the cloth and the pressure of the rollers are varied according to the quality of the goods, and the particular feel, lustre, and finish ultimately required. With such goods as must have subsequently a soft feel or "handle" —*e.g.*, Cashmeres, Coburgs, &c.,—no pressure at all is employed, the pieces being simply beamed tightly on the bottom roller.

(*b*) *Steaming.*—The pieces are unwrapped from the last crabbing roller (*i.e.*, from the cold water), and tightly wrapped on the perforated revolving iron cylinder G. Steam is admitted through the axis of this cylinder for the space of about ten minutes, or until it passes freely through the cloth. In order to submit every portion of the piece to an equal action of the steam, the process is repeated with the cloth tightly beamed on a second and similarly perforated roller G′, so that those portions of the cloth which were on the outside are now in the interior.

These perforated steam-cylinders are frequently quite separated from the crabbing machine, and then usually rest on a steam nozzle in a vertical or horizontal position.

(*c*) *Scouring.*—The cloth, being now "set," as it is technically termed, is scoured for half-an-hour or more, with soap solution at 40°—50° C. in the "Dolly" or "open width" machine, above described.

The sequence of operations as here given, although frequently employed, is not altogether rational.

The best results are obtained by crabbing and scouring simultaneously, and then steaming. To accomplish this, the boiling water in the crabbing troughs is merely replaced by a solution of soap, sodium carbonate, or other scouring agent. It is found that to steam the cloth in its oily state exercises some injurious action, and renders it liable to contract dark stains during mordanting, especially if stannous mordants are employed. It is possible that the oil is more or less decomposed, and a portion becomes fixed on the fibre.

68. **Bleaching of Wool.**—Wool is generally bleached either in the form of yarn or cloth, but only when it is intended to remain white, or if it has to be dyed in very light delicate colours. The bleaching agent universally adopted is sulphur dioxide. According to the state in which it is applied, either in the form of gas or dissolved in water, one may distinguish between "gas bleaching" and "liquid bleaching," and of these the former is more generally employed. In recent years that excellent bleaching agent, hydrogen dioxide, has become an article of commerce, and no doubt would be more largely used in woollen bleaching than it is at present, if only it were less costly.

Gas Bleaching, Stoving, or Sulphuring.—Yarn is first scoured and well washed, then suspended on poles and placed in the sulphur stove—a spacious brick chamber which can be charged with sulphur dioxide. The necessary amount of sulphur (in the proportion of 6—8 per cent. of the wool to be bleached) is placed in an iron pot in one corner of the chamber, and ignited by inserting a hot iron; the chamber is then closed, and the moist yarn is left exposed to the action of the gas for six to eight hours, or even overnight. Afterwards the chamber is thoroughly ventilated; the yarn is removed and well washed in water.

Heavy woollen cloth, such as blanketing, is treated in exactly the same manner as yarn, but with thin material—*e.g.*, merino, &c.—the operation is preferably made continuous, by adopting the arrangement of stove shown in Fig. 39. It is provided internally with a wooden frame, having rollers above and below. The roof should be lined with lead, and heated with steam pipes, in order to prevent condensation. The stove is charged with sulphur dioxide as already described, or, preferably, the sulphur is burnt in a separate furnace, and the gaseous product is led underneath the perforated tile floor of the stove. The cloth is introduced through a narrow slit in the wall; it then passes, as indicated,

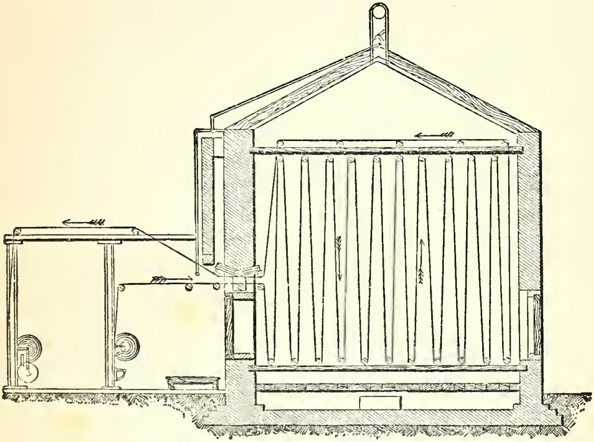


Fig. 39.—Sulphur Stove for Woollen Cloth Bleaching.

under and over the rollers, and passes out again by the same opening. The number of times the cloth is passed through the stove varies according to the appearance of the cloth.

In *liquid bleaching*, the woollen material is worked and steeped for several hours either in a solution of sulphurous acid or in a solution containing sodium bisulphite (5—50 grams per litre), to which an equivalent amount of hydrochloric acid has been added; it is afterwards thoroughly washed. A better method, however, is that in which the wool is treated with sodium bisulphite and hydrochloric acid in separate baths, whereby the sulphurous acid is generated within the fibre, and, being in the nascent state, acts more powerfully upon the colouring matter of the wool. Goods which have to remain white are tinted with some blue or bluish-violet colouring matter (*e.g.*, ground indigo, indigo-extract, aniline blue, &c.), either before or after the bleaching operation, in order to counteract the yellow colour of the wool which is so apt to return. The principle here applied is that of the complementary colours, which when mixed in due proportion produce white light. Blue is complementary to yellow.

The bleaching action of sulphur dioxide is most probably due to its reducing action upon the natural yellow colouring matter of the wool; another explanation, however, is that it combines with the latter to form a colourless compound. Certain it is that the effect is by no means permanent; frequent washing of bleached wool in alkaline solutions always tends to restore the yellow appearance of the fibre. Either oxidation is thus induced, or the colourless sulphite is decomposed, and the original colouring matter is precipitated on the fibre.

The agent *par excellence* for liquid bleaching is hydrogen dioxide (H_2O_2). Even yellow-coloured wool is bleached by it to a white, possessing a brilliancy and purity unattainable by the ordinary methods. The woollen material is steeped for several hours in a dilute and slightly alkaline solution of commercial hydrogen dioxide and afterwards well washed, first with water acidulated with sulphuric acid, and afterwards with water only.

CHAPTER VIII.

SILK SCOURING AND BLEACHING.

69. Object of Scouring Silk.—The object of scouring silk is to remove from the raw fibre a greater or less proportion of the silk-glue which envelops it, and thus to render it lustrous and soft, and better fitted for the operation of dyeing. According to the amount of silk-glue removed, the product of the scouring operation may be either *boiled-off silk*, *souple silk*, or *écru*, for each of which, indeed, a different treatment is necessary.

70. Boiled-off Silk is the name given to silk from which practically the whole of the silk-glue has been removed. It exhibits most fully the valued properties of lustre, softness, &c. Two operations are necessary for its production, namely, "stripping" and "boiling-off."

(*a*) *Stripping or Ungumming* (Fr., *dégommage*).—The object of this operation is to soften the silk, and to remove the great bulk of the silk-glue and also the colouring matter. The hanks of raw silk are suspended on smooth wooden rods, and worked by hand in rectangular copper troughs, in a solution of 30—35 per cent. soap, heated to 90°—95° C. When the water is very calcareous, the silk is first rinsed in a weak, tepid solution of sodium carbonate. The best plan is to correct the water previously. Rinsing in dilute tepid hydrochloric acid before ungumming is also good, since it removes calcareous and other mineral matters from the silk, and prevents their action in the soap bath. Weighted écru silks cause great inconvenience in the ungumming: the soap bath is precipitated, the fibre becomes tarnished and sticky, and the ungumming is rendered difficult and incomplete.

During the stripping operation the silk at first swells up and becomes glutinous, but, after a short time, when the silk-glue dissolves off, it becomes fine and silky. It is best, especially when the silk is intended for whites or delicate colours, to work it successively in two or three separate baths, for about twenty to twenty-five minutes in each, and to pass fresh lots of silk through in regular order. When the first bath becomes charged with silk-glue it is renewed, and then employed as the last bath. Each soap bath should be utilised to the fullest extent compatible with excellence of result. It is well to bear in mind that too prolonged contact with boiling soap solution is not good, since a little of the colouring matter of the glue is apt to be attracted by the fibre, and the silk loses substance, strength, and purity of white. The waste soapy and glutinous liquid obtained is called "boiled-off" liquor, and serves as a useful addition to the dye-bath when dyeing with the coal-tar colours.

After "stripping," the hanks are rinsed in water, in which a small quantity of soap and sodium carbonate has been dissolved.

(*b*) *Boiling-off* (Fr., *la cuite*). — For the purpose of removing the last portions of silk-glue, &c., and to give the silk its full measure of softness and lustre, it is now placed in coarse hempen bags, technically called "pockets," about 15 kilograms in each, and boiled from half an hour to three hours (according to the quality of the silk) in large, open copper vessels, with a solution of 10 — 15 per cent. of soap. The silk is then rinsed in tepid water, rendered slightly alkaline by the addition of sodium carbonate in order to prevent the precipitation of lime soap on the silk. It is finally washed well in cold water. The waste soap liquor may be used for "stripping." For some articles, the silk is boiled on wooden rods and not in pockets.

The soap employed, both for "stripping" and for "boiling-off" should be of the best quality. Other things being equal, those soaps are to be preferred which wash off most readily, and leave an agreeable odour. When, however, the silk has subsequently to undergo a number of soaping and other operations—*e.g.*, in weighted blacks—the odour of the soap used in boiling-off is of little consequence. Oleïc acid soap may be recommended in such a case, but for silk destined to be dyed in light colours or to remain white, a good olive-oil soap is preferable.

By scouring with soap in the above manner, Japanese and Chinese silks lose 18 — 22 per cent. of their weight and European silks 25 — 30 per cent.

Stretching (Fr., *étirage*).—When the silk is well softened during the stripping process, but not really ungummed, it may be conveniently stretched to the extent of 2 — 3 per cent. without injury; indeed, it acquires increased lustre by stretching. The operation may be performed either by the lustreing or the stringing machine.

Stoving.—When the silk is intended to remain white, or is to be dyed pale colours, it is bleached by exposing it in a moist condition to the action of sulphurous acid in closed chambers. The operation, which lasts about six hours, may be repeated two to eight times, according to the nature of the silk. Ten kilograms of silk will require about half a kilogram of sulphur. After stoving, the silk is well washed till free from sulphurous acid. For reference to the bleaching with a mixture of nitric and hydrochloric acids, see next page.

71. **Souple Silk** is silk which has been submitted to certain operations, to render it suitable for dyeing, &c., without causing it to lose more than 4 — 8 per cent. of its weight. The object of soupling is, indeed, to give to raw-silk, if possible, all the properties of boiled-off silk, with the least loss of weight; considerable perfection has already been attained in this direction. Souple silk is not so strong as boiled-off silk, and is used for only tram.

The process of soupling consists essentially of two operations, first, the *softening ;* and second, the *soupling* proper. With yellow silk, and whatever is intended to be dyed light colours, the operations of *bleaching* and *stoving* intervene.

(*a*) *Softening.*—The raw silk is worked for one to two hours in a solution of 10 per cent. soap, heated to 25° — 35° C. The object of this operation is to soften the fibre, and remove the small quantity of fatty matter present, so as to facilitate the operations which follow.

(*b*) *Bleaching.*—The silk is worked in stone troughs for eight to fifteen minutes in a dilute solution of aqua-regia 4° Tw. (Sp. Gr. 1·02), heated to 20° — 35° C. It is afterwards washed well till free from acid.

The aqua-regia is prepared by mixing together five parts, by weight, of hydrochloric acid, 32° Tw. (Sp. Gr. 1·16), with one part of nitric acid, 62° Tw. (Sp. Gr. 1·31), and allowing the mixture to stand for four or five days at a temperature of about 25° — 30° C. Before use it is diluted with fifteen volumes of water. For the aqua-regia may be substituted sulphuric acid saturated with nitrous fumes, or a solution of the so-called "chamber-crystals" obtained in the manufacture of sulphuric acid.

The silk must not be worked too long in the acid liquid, otherwise the nitric acid causes it to contract a yellowish tint which cannot be removed. The moment the silk has acquired a greenish-grey colour it should be withdrawn from the bath, and well washed with cold water.

(*c*) *Stoving.* — This operation is similar to that already described (*see* previous page). It renders the silk hard and brittle. Without removing the sulphurous acid, however, it is at once submitted to the following operation.

(*d*) *Soupling* (Fr., *assouplissage*).—The silk is worked for about an hour and a half, at 90°—100° C., in water, containing in solution 3 — 4 grams cream of tartar per litre. The silk becomes softer and swells up, and being thus rendered more absorbent, it is better adapted for dyeing. The operation of soupling is a somewhat delicate one, and needs considerable judgment and practice. The solution must not be too hot, nor must the immersion of the silk be too prolonged, otherwise the loss in weight is excessive, and the result is unsatisfactory. After soupling, the silk is finally worked in a bath of tepid water. Souple-silk will bear warm acid baths subsequently, but not alkaline or soap baths beyond a temperature of 50°—60° C., otherwise it loses silk-glue, and is more or less spoiled. The operation of soupling is sometimes performed on raw-silk which has been previously submitted to other operations, as, for example, in the dyeing of so-called black souples.

A satisfactory explanation of the theory of soupling has not yet been given. The cream of tartar probably acts as an acid salt merely, and although it gives the best results, it can be replaced by a solution of sodium or magnesium sulphate acidified with sulphuric acid, or even by very dilute hydrochloric acid. It is curious that silk is rendered less tenacious by soupling than by boiling-off.

72. **Ecru Silk** is raw-silk which at most is submitted to washing, with or without soap, and bleaching. The loss of weight varies from 1 to 6 per cent. Unbleached écru silk is only dyed in one or two different shades of black.

73. **Bleaching of Tussur Silk.**—This may be accomplished according to the method proposed by M. Tessié du Motay, in which barium binoxide is the agent employed. Free baryta hydrate is first removed from the binoxide by washing the latter with cold water, and a bath is then prepared, containing binoxide in the proportion of 50 — 100 per cent. of the weight of silk to be bleached.

The silk is washed for about an hour in the bath heated to 80° C., then washed and passed into dilute hydrochloric acid, and washed again. If the white is not good, the operations are repeated, or one may also complete the bleaching by washing the silk in a solution of potassium permanganate and magnesium sulphate, and afterwards in a solution of sodium bisulphite, to which hydrochloric acid has been added.

Although barium binoxide is little soluble in water, at the temperature of the bleaching bath it gives up oxygen to the fibre by degrees, even without the addition of any acid, so that the bleaching takes place gradually. During the immersion the silk also absorbs a certain amount of the binoxide, probably as hydrate, so that on the subsequent passage into acid there is liberated within the fibre hydrogen dioxide, which, being in the nascent state, bleaches to the best effect.

The chief difficulty of the process consists in the fact that, by long contact with the barium binoxide the silk becomes dull, harsh, and tender, but with care the process can be made to yield excellent results, and it is, indeed, already adopted in practice. Hypochlorite of ammonia has been employed, but with less success. The very best bleaching agent for Tussur and also Mulberry silk is hydrogen dioxide. It is applied in the same manner as indicated on p. 114 for wool.

Tussur silk is bleached for the purpose of dyeing it in light colours.

varies according to the character of the rock or soil through or over which it has passed.

If the geological strata are composed of such hard insoluble rocks as granite and gneiss, the water remains comparatively free from impurities, and whether it flow as a river or rise as a spring, it will be what is termed a "soft" water.

If, on the contrary, the water during its subterranean course meets with rocks containing such a soluble constituent as rock-salt, it becomes brine; if it encounters a stratum of lime-stone, oolite, chalk, new red sandstone, &c., it dissolves a certain portion of it, and becomes magnesian or calcareous, and constitutes on its reappearance what is called a "hard" water. Common limestone being generally of a less permeable nature than magnesian limestone, does not yield such hard water as the latter. Again, if the water passes through or over rocks containing iron in some form or other, it takes up some of the iron and becomes a so-called "chalybeate" water. When the rain-water drains from boggy moorland, a certain portion of the more or less decomposing vegetable matter dissolves, and the water is usually brown-coloured.

The natural impurities of water which concern the dyer may be either *suspended* or *dissolved*, and of these the latter are the most important. A constant supply of *clear* water is certainly an indispensable requisite, but the means of purifying muddy water are comparatively simple, and the chemical nature of the suspended matter generally possesses little or no interest. The *dissolved* constituents of water, however, are equally, or even more, injurious, and to effect their removal is much more difficult, involving as it does the employment of chemical means of purification. As a general rule, river water contains the largest amount of suspended and vegetable matter, and the least amount of dissolved constituents, whereas spring and well water bear the opposite character.

75. Calcareous and Magnesian Impurities.—These are at once the most frequently occurring, and the most injurious of all impurities. They are usually present as bicarbonates, less commonly as chlorides and sulphates. The latter are generally less injurious than the former.

The presence of *lime* is shown, if the addition of a solution of ammonium oxalate to the water in question gives a white precipitate of calcium oxalate. On evaporating such a water to a small bulk it becomes turbid. If, then, the addition of hydrochloric acid produces effervescence, and renders the solution again perfectly clear, it is an indication that all the lime is present as bicarbonate. If there is no effervescence and no clearing, it is probably all present as sulphate. Effervescence and partial clearing denote the presence of both sulphate and carbonate. Should there be no turbidity on evaporation, lime is either absent altogether, or it is probably present as chloride or nitrate.

The presence of *magnesia* is detected, after lime and alumina have been removed by means of ammonia and ammonium oxalate. The filtered liquid is concentrated by evaporation, and mixed with a solution of phosphate of soda and ammonia; magnesia is present if a white crystalline precipitate is thereby produced. The separation, however, of lime and magnesia has little or no importance for the dyer.

The presence of *bicarbonates* is further detected by the addition of a clear solution of lime-water producing a white precipitate.

Sulphates are present if an addition of hydrochloric acid and barium chloride gives a white precipitate.

A white curdy precipitate, which is produced on adding nitric acid and silver nitrate, denotes the presence of *chlorides*.

The injurious influence of magnesian and calcareous water cannot be overrated, and very specially because of its property of precipitating soap solutions. Hard water only produces a froth or lather with soap after the whole of the calcium and magnesium compounds present have been precipitated as insoluble lime and magnesia soaps, the latter of which may be distinguished from the former by their more objectionable curdy character.

By employing a soap solution of a standard strength, it is possible to calculate approximately the amount of calcium and magnesium compounds present. Details of this method of determining the hardness of water (Clark's) are given in most text-books of chemical analysis.

It is well to note that, according to Clark's scale, a water with one degree of hardness contains one grain calcium carbonate per gallon, but after the newer scale of Frankland, one degree of hardness signifies that the water contains one gram of $CaCO_3$ in 100,000 grams water. To reduce the degrees of the latter to those of Clark's scale it is simply necessary to multiply by seven-tenths.

In all those operations where large quantities of soap are employed, it is evident that the use of a hard water entails a considerable loss of soap. One kilogram of CaO decomposes about 15·5 kilograms of ordinary soap containing 30 per cent. of moisture. After making a soap-analysis of the water, and knowing the quantity of the water employed, it is easy to calculate the annual loss of soap (about one-sixth) occasioned by the hardness of the water. Taking the monthly consumption of soap in London as 1,000,000 kilos., it is estimated that the hardness of the Thames water causes an expenditure of 230,000 kilos. more soap per month than would be required if soft water were used.

This is, however, by no means the only disadvantage. The precipitated earthy soaps are more or less of a sticky nature, and adhere so tenaciously to the fibre that they cannot be removed by ordinary technical processes. In the scouring of wool, or of silk, they render the fibre more or less impermeable, so that neither mordant nor colouring matter can be afterwards properly fixed thereupon, and irregular development of colour results.

When the soap solutions are applied *after* dyeing—*e.g.*, in the clearing of Turkey-red, milling of woollen fabrics, &c.—the precipitated earthy soaps may impart to the finished fabric a pale greyish "bloom," or an unnatural lustre, and altogether ruin both the brilliancy of the colour and the value of the fabric.

In some cases earthy soaps may act injuriously by playing the rôle of mordants. It would be dangerous, for example, to employ soap in the bleaching of calico for printing purposes, or to re-dye printed calicoes after soaping, since any lime-soap precipitated on the fabric would attract colouring matter, and cause the white ground to be stained.

Hard water is also injurious in the dye-bath, because it only imperfectly extracts the colouring matter from the dye woods employed. Some colouring matters—Alizarin Blue, Cœruleïn, &c., also Catechu and Tannin matters—produce insoluble compounds with the alkaline earths, and may thus be precipitated and rendered inactive.

It must not be forgotten, however, that the presence of a certain limited amount of lime is beneficial, nay, even necessary, in dyeing with some colouring matters—*e.g.*, Alizarin, Logwood, Weld, &c.—but in such cases even, it is always preferable to have a pure water, so that one may add the most suitable form and amount of lime salt.

Hard water has generally the effect of dulling the colours obtained from many colouring matters, both during the dyeing and the subsequent washing processes. When the hardness is due to the presence of earthy bicarbonates, it retards or even prevents the dyeing of such colours as are produced only in an acid bath, *e.g.*, cochineal scarlet.

Such water acts injuriously also on solutions of certain mordants—like those of aluminium, iron, &c.—by

neutralising a portion of their acid and precipitating basic salts, thus rendering the mordanting bath less effective.

In some cases of mordanting, however, water containing earthy bicarbonates is to be preferred to pure water, since it fixes a much larger quantity of insoluble basic salt on the fibre, as, for example, in the washing of silk after mordanting with basic ferric sulphate, and with aluminium or tin mordants.

Water rich in earthy bicarbonates is not suitable for the solution of many of the coal-tar colours, such as Methyl Violet, &c. A portion of the colour-base is precipitated as a tarry mass, and not only is colouring matter wasted, but goods dyed in such solutions are apt to be spotted.

76. Ferruginous Impurities.—These are also very objectionable in dyeing operations. They are to be looked for in water which is derived from disused coal-pits, iron-mines, iron and aluminous shales, &c. Surface water draining off moorland districts and passing over ochre-beds also contains iron, evidence of which is seen in the brown ferric oxide deposited on the stones in the stream. All such water should be rigorously avoided.

To test for the presence of iron, evaporate some of the water in a clean porcelain basin. If a reddish brown deposit is thereby produced, this must be collected, dissolved in a little hydrochloric acid, and thoroughly oxidised by heating, with the addition of a little potassium chlorate. The solution is diluted and cooled, and a solution of potassium ferrocyanide, or thiocyanate, is added. If iron is present, a blue precipitate or red coloration, respectively, is thereby produced.

The iron being usually present as bicarbonate, acts upon soap solutions after the manner of the analogous calcium and magnesium compounds, and similar or even worse results ensue.

In wool-scouring, cotton-bleaching, and other operations where alkaline carbonates are used, ferric oxide is precipitated upon the fibre. With such goods it would be quite impossible to dye bright colours subsequently —*e.g.*, alizarin reds, &c.—and all colours, indeed, suffer more or less. Bleached fabrics acquire an unpleasant yellowish tinge, and are rendered quite unsaleable.

77. **Alkaline Carbonates as Impurities.**—Water containing sodium carbonate is frequently met with in districts where the supply is derived from wells which penetrate the lower beds of the Coal Measures. This alkaline condition is detected by means of red litmus-paper.

Such water is by no means detrimental in wool scouring, or in operations where alkaline carbonates are nominal constituents of the bath, if other injurious constituents are absent; but for purposes of mordanting, dyeing, and washing of dyed goods, it is, if possible, more injurious than the water containing earthy carbonates. When no other water is to be had, it must for such operations be carefully neutralised with sulphuric or acetic acid.

78. **Acid Salts and Free Acids as Impurities.**—Water draining from moorland districts contains what are usually termed *peaty acids*, and since these attack iron very readily, they may indirectly cause serious injury.

Water derived from shale beds containing pyrites and situated near the surface, becomes contaminated with ferrous sulphate. On exposure to air this salt oxidises, ferric oxide is deposited, and the water contains free sulphuric acid. Blue litmus-paper serves to detect the presence of this impurity.

Such water is unsuitable for scouring operations, since it decomposes and wastes the detergents used. If soap is employed, fatty acid is liberated and liable to be fixed upon the fibre. In dyeing operations acid water is equally injurious. If such water cannot be avoided, it must be carefully neutralised with carbonate of soda.

79. **Organic Impurities.**—These as they exist in moorland streams have not been found in practice to be injurious, unless the water is thereby so deeply coloured

as to stain the woollen or other fibre, which is to be dyed light shades only, or is intended to remain in the bleached condition. In the absence of inorganic reducing bodies the presence of organic matter is determined by adding a solution of permanganate of potash sufficient to impart a pink colour, acidifying with sulphuric acid, and then boiling. If organic matter is present the solution is decolorised.

80. Sulphuretted Hydrogen as an Impurity.—This is only occasionally met with, and arises through the decomposition of gypsum by organic matter. Such water is to be rejected, since, when iron, tin, copper, and lead mordants are used, sulphides of these metals are formed, and cause black or brown stains.

This impurity is detected by slightly acidifying the water with acetic acid and placing it in closed flasks in a warm place for some time. A strip of filter paper moistened with lead acetate is fixed above the surface of the liquid. The formation of brown lead sulphide on the filter paper denotes the presence of sulphuretted hydrogen.

Specially injurious are the impurities which may come from establishments situated higher up the stream, *e.g.*, paper-works, chemical-works, bleach-works, &c. Hence the dyer, whose only source of supply is a river running through a manufacturing district, must be specially vigilant, for although the pollution of rivers by waste products, &c., from various manufactories may be forbidden, the compliance with this restriction is beset in many instances with enormous difficulties which, indeed, can only be partially overcome.

81. Correction and Purification of Water.—Pure water is certainly one of the first requisites for all operations of bleaching and dyeing. Unfortunately it is at the disposal of few manufacturers, and the increasing injury thus caused has not always met with the attention it deserves. Directors of bleach and dye works will find this subject as difficult as it is interesting and important. Although it is comparatively easy to purify, or at least to correct, small quantities of water, the technical problem of readily purifying such large supplies of water as are necessary for dyeing, &c., is surrounded with difficulties. The purification of water usually comprises both a mechanical and a chemical treatment.

82. **Mechanical Purification.**—Whenever the land is suitable, the water is collected and allowed to settle in large reservoirs, even if only for the purpose of storage. When possible, several reservoirs are maintained, and it is well to pass the water from one to the other in such a manner as to expose it as much as possible to the air—for instance, by a staircase cascade. Finally the water should be passed through filter-beds of sand. During the exposure to air, in this manner, a partial chemical purification will take place in water containing calcium, magnesium, or iron bi-carbonates; a portion of the solvent carbonic acid is lost and the carbonates are precipitated.

The most favourable circumstance is that in which the works are placed upon the bank of a river flowing from a lake situated immediately above, so that neither heavy rains nor melting snow will render the water turbid.

83. **Purification by Boiling.**—Reference has already been made to the convenient classification of "soft" and "hard" waters. The latter may be sub-divided into those which are *temporarily hard*, and those which are *permanently hard*, although most waters combine both properties.

A water possessing *temporary hardness* becomes soft by mere boiling, if this is sufficiently prolonged, since such hardness is due to magnesium, calcium, or iron bi-carbonates. The effect of boiling is to expel one-half of the carbonic acid, and thus to precipitate the insoluble mono-carbonates produced. Since the softening effect takes place only gradually, the boiling should be continued for 20—30 minutes at least. It is scarcely necessary to add that this method of purification is far too costly to serve for large quantities of water.

A water which is *permanently hard* derives this property from the presence of sulphates of the above-mentioned metals; hence, in this case, boiling has no softening influence; on the contrary, the hardness is increased through the concentration of the water, and other modes of purification must be adopted.

84. Chemical Purification.—As to the purification or correction of water by chemical means, one element of difficulty is the inconstancy of the composition of the water. Heavy rain and melting snow dilute it, while hot summer weather concentrates it, especially in small rivers. Whenever it is impossible to keep pace with varying conditions of this kind by making frequent analyses of the water, it is advisable, in the absence of purification or correction on a large scale, to add to the water such agents as are not specially injurious, even if added in slight excess. In many cases it suffices to neutralise as carefully as possible the alkalinity of a water arising from the presence of earthy bi-carbonates, by the addition of acetic acid, *e.g.*, in most cases of dyeing, or for the purpose of dissolving coal-tar colours. An old method of purifying small quantities of water which is still often used by silk and woollen scourers, &c., is to boil the water with the addition of a little soap, with or without the addition of sodium carbonate, and to skim off the earthy soaps thrown to the surface. Apart from its expense, this method is unsatisfactory, since the major portion of the earthy soaps, &c., remains disseminated in the water in a finely-divided state. Water corrected in this manner is necessarily left in an alkaline condition from the alkali of the soap remaining behind, and of course the amount of alkaline carbonate left is equivalent to that of the earthy salts removed, thus

$$\underset{\text{Calcium bi-carbonate.}}{CaH_2(CO_3)_2} + \underset{\text{Soap.}}{2C_{18}H_{33}O_2Na} = \underset{\text{Lime-soap.}}{Ca(C_{18}H_{33}O_2)_2} +$$

$$\underset{\text{Sodium carbonate.}}{Na_2CO_3} + CO_2 + \underset{\text{Water.}}{H_2O.}$$

The dyer's method of adding alum to the water of the mordanting or dye-bath, and then boiling and skimming off impurities which rise to the surface, is even more uncertain, and is strongly to be deprecated.

85. Purification with Lime. Clark's Process.—Since calcium and magnesium carbonates are soluble in water only by the presence of carbonic acid, the natural remedy is to employ some means which will rapidly and effectively remove or absorb the latter. In 1841, Dr. Clark proposed calcium hydrate or slaked lime as the cheapest and most suitable agent for this purpose, and his method or some modification of it is still generally adopted. The following equation explains the theory of the process :—

$$\underset{\substack{\text{Calcium}\\\text{bi-carbonate.}}}{CaH_2(CO_3)_2} + \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{Ca(OH)_2} = \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{2CaCO_3} + 2H_2O.$$

In carrying out the method here expressed, many practical difficulties are met with, and constant skilled oversight is necessary to insure success.

Only the temporary hardness is removed, and not even this completely. A small residuum of chalk always remains in solution. It is quite possible, however, to remove 10-11ths of the whole temporary hardness, as well as iron salts and much organic matter. Experiments on a large scale have proved that, by the lime process, water of 23° hardness can be reduced to 7°, of 15° to 3° or 4°, and so on.

It is best to employ clear lime-water for correction, since this possesses a known constant composition. The amount of such lime-water which it is necessary to employ may be calculated after making an analysis of the water, or may be determined by actual experiment. If the number of degrees' hardness (Clark's scale) is divided into 130 or 150, the number obtained will approximately represent as a rule the number of litres of water which can be softened by the addition of one litre of lime-water.

Clear lime-water may be replaced by milk-of-lime, if the latter is carefully applied. Excess of lime in the corrected water is readily detected by adding a little of it to a filtered decoction of cochineal. Such excess changes the yellowish-red colour of the solution to a violet. Other delicate alkali-indicators may also be adopted.

In working Clark's process as originally devised, large tanks or reservoirs are requisite. It is best to have at least three—one into which to run the water and lime and to allow the precipitated chalk to settle for about 16 hours; another from which clear and previously corrected water can be drawn; and a third as a reserve during cleansing operations. Each reservoir should hold at least a day's supply.

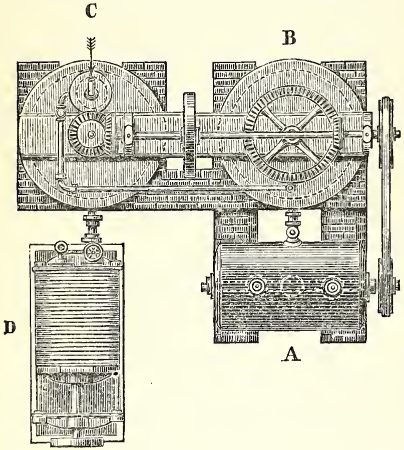


Fig. 40.—Plan of Porter-Clark's Apparatus for Softening Water.

86. Purification with Caustic Soda.—For purposes of scouring, or where a slightly alkaline water is not prejudicial, caustic soda may be conveniently substituted for quicklime, since its solution can so readily be made of a standard strength and added in the requisite amount to the water to be corrected:—

$$CaH_2(CO_3)_2 + 2\ NaHO = CaCO_3 + Na_2CO_3 + 2\ H_2O.$$

In this case, of course, exactly the same amount of sodium carbonate remains in the corrected water as if the purifying agent used had been soap. It is well to heat the mixture to 50° C. in order to cause more rapid settling of the precipitate. Mechanical impurities, also iron, aluminium, and earthy phosphates are completely thrown down.

Permanent as well as temporary hardness is removed by the use of caustic soda, since the calcium and magnesium sulphates present are decomposed by the sodium carbonate produced in the above reaction.

Should the water corrected in this manner be required for purposes where alkalinity is to be avoided, it can be readily neutralised before use.

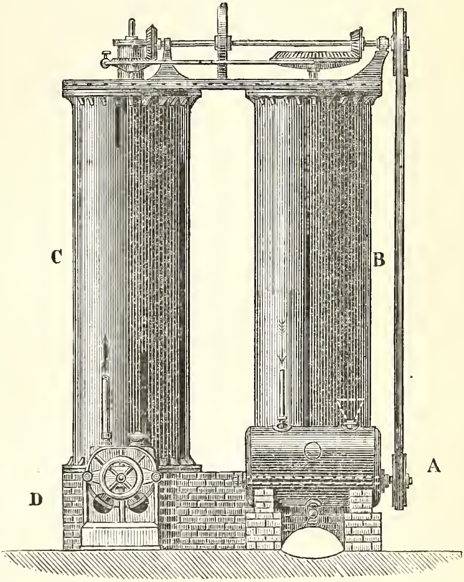


Fig. 41.—Porter-Clark's Apparatus for Softening Water (elevation).

87. Porter-Clark Process.—The essential improvement effected by this process is a saving of space, time, and labour, through the application of machinery to the ordinary Clark's process.

Figs. 40 and 41 give plan and elevation of an arrangement for supplying over 6,000 litres of softened water per hour, but there is practically no limit to the amount which may be supplied if the apparatus is made large enough.

The lime-water is prepared in the small horizontal cylinder A, by constantly churning up slaked lime with water admitted under pressure direct from the reservoir or main. By a pipe midway in the height of the churn, the more or less saturated lime-water (a saturated solution contains about 1·4 grams of lime per litre), and with some lime in suspension, is led into the large cylindrical vessel B, where the lime and water are kept in slight agitation, to assist in completing the saturation. As the lime-water ascends, the particles of lime in suspension gradually settle out, and tolerably clear lime-water passes out at the top into the cylinder C, where it is continuously mixed with the water to be purified, in accurately determined proportions. The supply of each is regulated by valves furnished with dial plate and index. A brisk agitation is maintained in the mixing cylinder C, in order to facilitate the chemical reaction taking place. When this is completed, the chalky water is forced through the filter-press D, wherein the carbonate of lime acts as a medium of filtration, and the clear water thus obtained is at once fit for use.

If it be desired to remove both permanent and temporary hardness by means of the above apparatus, carbonate of soda, or caustic soda, must be used in addition to the lime.

88. Gaillet and Huet's Process.—The agents of purification here adopted are lime and caustic soda, and the cost does not exceed, say, one farthing per 1,000 litres of softened water.

This apparatus differs essentially from all others by the simple but effective means adopted for separating and removing the precipitated impurities without in any way choking the purifier or retarding the delivery of water.

Fig. 42 gives a perspective view of a complete apparatus capable of purifying about 200,000 litres of water per day. The purification takes place in the large square clarifying, or precipitating, tank A, which forms the body of the apparatus, and which is shown separately in Fig. 43, a portion of the casing being there removed

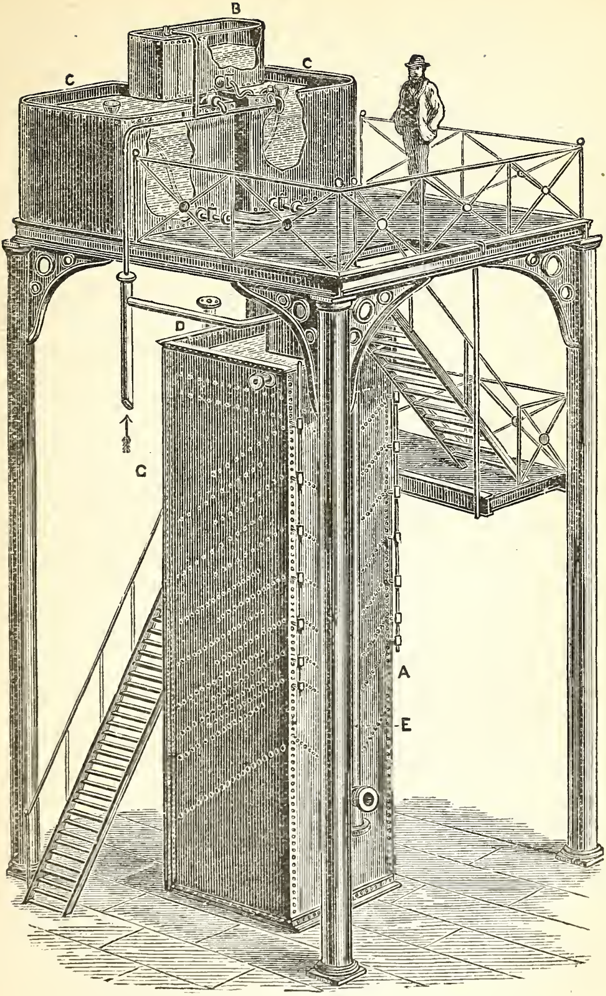


Fig. 42.—Gaillet and Huet's Apparatus for Softening Water.

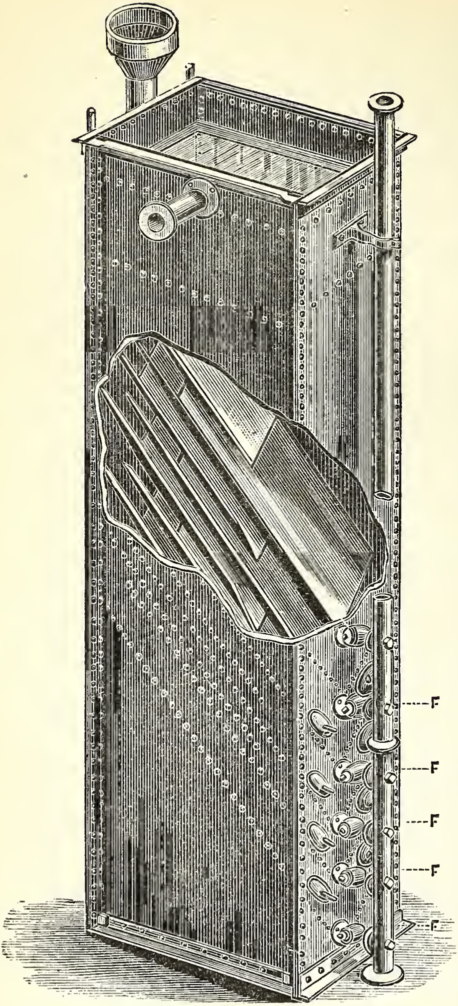


Fig. 43.—Gaillet and Huet's Precipitating Tank.

to show the interior arrangement. Instead of passing downwards through filtering screens, which would soon become clogged and retard the flow, the water, after having been mixed with the precipitating reagents, enters at the bottom of the tank, A, and rises slowly towards the top, following a zig-zag course in the shallow spaces between a number of V-shaped diaphragms, inclined at an angle of 45°, and riveted alternately to opposite faces of the tank as also to the two adjacent sides. All the diaphragms shelve at the same angle towards the same face of the tank, where they lead to a series of mud cocks, F.

Above the clarifying tank are situated smaller tanks, in which the precipitating reagents are dissolved. Tank B contains the solution of caustic soda, of which the required quantity is run off into one of the tanks, C, in which lime has been dissolved in water. The liquid is allowed the requisite length of time to settle, the other tank, C, being meanwhile in use. The clear soda-lime solution thus obtained is run off at a regulated rate, and mixes with the water to be purified entering at D, in a special tank situated above the clarifying tank, A, and immediately below the raised platform. The turbid water falls through the pipe E, enters the clarifying tank at the bottom, and at once assumes an upward motion. As the section of the tank, A, is very large, and that of the supply pipe, D, very small, the water naturally rises very slowly and gently, allowing the precipitate to settle almost as if the water were at rest. The purpose of the V-shaped diaphragms will now be apparent. The water has to pass slowly between them in shallow layers, and as the solid particles have but a few inches to fall, they readily settle upon the diaphragms, which represent, indeed, a very large precipitating area in a limited space. As the latter are V-shaped, the deposit slides down into the angle towards the mud cocks, F, through which it is discharged when necessary. The water meanwhile becomes gradually clearer as it rises, and is ultimately drawn off at the top, G, perfectly soft and limpid.

The process of purification is carried on automatically without the necessity of constant attendance or motive power. It need scarcely be added that the amount of soda-lime solution to be mixed with the water is determined according to the results of a careful analysis, previously made, of the water.

Other modifications of Clark's process are in vogue, differing chiefly by the mode of effecting the clarification of the water after mixing with the precipitating reagents, but the two processes described may be considered typical of the rest.

89. Purification of Water discharged from Dye-houses.—If it is necessary that the dyer should have pure water for the successful prosecution of his business, he ought to feel it his duty not to pollute the river, from which he possibly receives his supply, with injurious discharges, to the annoyance and loss of his less-favoured neighbours lower down the stream.

Not only are the waste liquids from dye-works for the most part highly coloured, but they contain large quantities (over 1·5 grams per litre) of organic and inorganic matter, both suspended and dissolved. Should the dye-works situated on the banks of a small stream be numerous, the latter generally assumes a turbid, inky appearance; its bed is gradually impregnated with decomposing organic matter, putrescent odours are given off, the water is poisoned, and the stream becomes practically a large open drain, disagreeable to the sight and more or less noxious to health.

One of the simplest modes of mitigating this evil is to conduct all the refuse waters resulting from the various operations of the works into two or more reservoirs, where they mix together and precipitate each other. The whole must be allowed ample time to settle, and only the clear water permitted to flow into the river. Where space is limited, filtering beds of coke, sand, &c., may take the place of settling reservoirs. The purification is rendered more complete, however, if additional precipitating agents are employed, *e.g.*, magnesium and calcium chloride, lime, &c. Of these, lime is perhaps the cheapest and the most generally efficacious; it neutralises acids, precipitates colouring matters, mordants, soapy liquids, albuminous matter, &c.

That such simple means can accomplish the end in view in a most satisfactory manner is exhibited in the large works of Mr. W. Spindler, at Cöpenick, near Berlin, in which are carried on all branches of dyeing, printing, and finishing, of silk, woollen, and cotton goods.

In this establishment, according to Caspari, all the refuse water flows into two large collecting reservoirs, where the suspended matter is allowed to settle. The supernatant water is shown by analysis to be strongly impregnated with salts of the alkalies and iron, together with tannin and extractive matter from dyewoods, fatty matter, colouring matter, &c. After being transferred to another reservoir, therefore, it is mixed with lime-water and a solution of calcium chloride; precipitation ensues, and the whole turbid mixture is pumped into still larger reservoirs, where it is allowed to settle. The clear water now obtained is found to be simply a hard water containing a small amount of organic matter, and is either used for purposes of irrigation or allowed to drain through the soil into the river.

The solid matter which has settled in the first collecting reservoirs is dried and calcined in gas retorts, and yields per 100 kilograms, 13—16 cubic metres of illuminating gas.

In bleach-works the refuse liquids consist of alkaline and soapy solutions, together with such as contain calcium chloride, traces of bleaching-powder, and free acids. Here are all the elements necessary to mutual purification, if allowed to mix together in due order and proportion; the calcium chloride will precipitate the soapy solutions, while the free acids will neutralise and precipitate the alkaline liquids and decompose the waste solutions of bleaching-powder.

It is impossible that any single method of purification should be applicable to all works, but the following description of a satisfactory process, devised by Messrs. R. and A. Sanderson and Co., of Galashiels, and adopted by all the woollen manufacturers of that town, will be of interest, and may indicate what ought to be done in this matter in woollen mills.

The effluent water from woollen dye-works consists partly of solid matter in suspension—*e.g.*, spent dye-woods, fragments of woollen fibres, &c.—and partly of soluble substances contained in the waste dye, mordant, and scouring liquors. The method of purification is of necessity, therefore, chemical as well as mechanical.

Fig. 44 gives a plan of the purification plant in use at Messrs. Sanderson's works, where upwards of 40,000 litres of waste scouring-liquor and about 120,000 litres of dye and acid magma water are treated daily.

In order to reduce as much as possible the amount of waste water to be purified, the soapy liquids from the yarn and piece scouring are used again in the wool-scouring. The refuse liquid from this operation is run through a sieve into the settling tank, A, whence it overflows at a given point into the large reservoir, B. From here it is pumped into the high level magma tanks, C (each of about 20,000 litres capacity), where it is thoroughly well mixed, by means of an air-pump, P, with a calculated quantity of sulphuric acid. After being allowed to settle, the supernatant acid liquid is run off into the tank, E, for further treatment. The precipitated magma of fatty matter is allowed to flow into the pit, D, the bottom of which is a drainer made up of ashes, spent dyewood chips, and sawdust. Here it is allowed to drain for about a week, the acid filtrate being also led

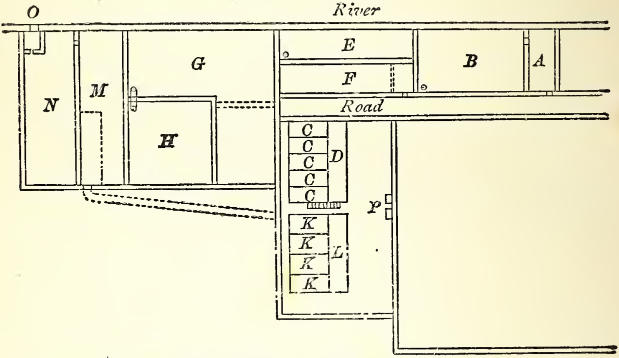


Fig. 44.—Plan of Purification Works for Waste Dye-liquors.

into the tank, E. The pasty magma is sold to oil-extractors and soap-makers.

The highly-coloured discharge from the dye-house passes through a sieve into the settling tank, F, whence it overflows into the large reservoir, G. In this reservoir the colouring matter of the spent dye-liquor, and the unexhausted mordants, partially combine and precipitate each other. Tank H contains slaked lime, well mixed with some dye-house liquor from tank G.

By means of the pump, P, definite proportions of acid magma water, from E (about one part), spent dye-liquor, from G (about three parts), and lime-water from H (about one part), are forced into the high level purification tanks, K, and there thoroughly well mixed. By this means the whole of the colouring matter is thrown down as a fine, flocculent precipitate. After being allowed to settle, the almost colourless supernatant water flows into the tank M, and the deposit is run off at intervals into the pit L, and there allowed to drain until it acquires such a consistency that it can be dug out and conveyed to the refuse heap. The water from the purification tanks, K, is slightly alkaline from excess of lime, but in the tank M it is neutralised by allowing it to mix with the slightly acid rinsing-water coming from the dye-house. Thus purified, the water overflows into the tank N, and passes through a filter into the river O, clear, neutral, and free from objectionable colour.

The following is an analysis of the effluent water by Crum Brown :—

Total solids in grams per litre		Turbidity	Colour	Ammonia in grams per litre		Analysis of inorganic solids in grams per litre	
Organic	Inorganic			Saline	Albuminoid		
0·13	0·78	1	3	0·003	0·002	$K_2Cr_2O_7$ . .	0·006
						Ca SO_4 . .	0·11
						Ca CO_3 . .	0·32
						Na_2SO_4 . .	0·29
						Na Cl . .	0·06

The turbidity is represented by the quantity of china clay (stated in grams per seventy litres), which, when added to pure water, gives a turbidity equal to that of the sample.

The colour is represented by the quantity of ammonia (stated in hundredths of a gram per seventy litres), which, when added to pure water, gives, with Nessler's reagent, a colour as nearly as possible agreeing with that of the sample. The colour of the effluent water is a faint brownish-yellow.

This analysis shows that, with the exception of the small quantity of potassium dichromate, the substances remaining in solution in the water discharged into the river, are the usual substances found in ordinary spring and river water.

In explanation of the above process, it may be stated that part of the lime used serves the purpose of neutralising the acid magma liquor, while the excess precipitates, from the waste mordant liquor, the hydrated metallic oxides, which at once combine with and precipitate any colouring matter present. It will be observed that, as far as possible, the waste materials from the various processes of manufacture are caused to aid in their mutual purification and removal from the water discharged into the river.

In the works of E. Schwamborn at Aachen, the refuse water from the washing of raw wool, and the milling and washing of cloth, is precipitated by lime. The composition of the air-dried precipitate is as follows:—

Water . . .	3·11	per cent.
Lime and ferric oxide	18·47	,,
Fatty matter . .	71·96	,,
Wool fibre, &c. .	6·46	,,

Mixed with coal, this precipitate serves for the manufacture of illuminating gas. Although in this method the potash salts of the raw wool are lost, it is estimated that, after deducting the working expenses, there is a net recovery of 30 per cent. of the value of the soap used in milling. In other works the precipitate is treated for the recovery of fat.

The economy which can be effected by the general adoption of some such methods as these, may be calculated from the statistics which give the weight of cloth milled each year in Europe as 500 million kilos., corresponding to about 100 million kilos. of lime-soap of the above composition.

THEORIES OF DYEING.

CHAPTER X.

ABOUT DYEING.

90. Materials and Colouring Matters.—The two most essential elements with which the dyer has to deal, are the material to be dyed and the colouring matter to be applied. With regard to the former, our attention is confined to the textile fibres, and it has already been shown that great differences exist between them, both as to their physical and their chemical properties. Not unnaturally, therefore, they might be expected to behave differently towards colouring matters. That such is really the case is readily shown by making the following simple dyeing experiment.

Three pieces of clean white textile material—wool, silk, and cotton—are immersed in a moderately strong aqueous solution of acid Indigo Extract, and are kept in continual movement by stirring, while the liquid is gradually heated to the boiling point. If the pieces are then taken out and well washed with water they present a remarkably different aspect; the wool and silk have become dyed, and appear pale or deep·blue according to the amount of colouring matter employed, while the cotton is not dyed, or, at most, becomes slightly stained. If the experiment is repeated with many other colouring matters—*e.g.*, Magenta, Methyl Violet, &c.—similar differences are noticed.

The real cause of this striking difference in behaviour towards colouring matters exhibited by the different textile fibres is still a matter of discussion. Several theories have been propounded, but none have gained general acceptance.

It is maintained by some that the animal fibres attract certain colouring matters by reason of chemical affinity, and that in the process of dyeing they actually combine with the soluble colouring matter to produce an insoluble coloured compound. Cotton, they say, does not become dyed because it has no affinity for such colouring matters. Such is the purely *chemical theory of dyeing.*

The opponents of this theory very properly urge as a vital objection to it, that two fundamental signs of chemical combination having taken place are entirely wanting, namely, the union of the fibre and colouring matter according to chemical equivalents, and the disappearance of the special properties of each.

Experiment proves that the animal fibres may attract either large or small amounts of Indigo Extract, and be properly dyed in both cases, the difference being simply one of intensity of colour. There is not the slightest appearance of a combination according to molecular proportions, as in the formation of Prussian Blue by the mutual reaction of ferric chloride and yellow prussiate of potash.

As to the second point of the objection, no doubt the *soluble* Indigo Extract attracted by the fibre has apparently become more or less *insoluble* in water, but it can be readily removed—*e.g.*, by heating with a dilute solution of carbonate of soda—with all its properties unchanged, and the decolorised fibre is also exactly the same as before.

Those who adhere to the *mechanical theory of dyeing* explain the foregoing facts, by stating that the animal fibres have become dyed by reason of a purely physical attraction exerted between the Indigo Extract and the said fibres. The latter, they say, are very porous or absorbent bodies, the colouring matter has penetrated the substance of the fibre, and is there retained in an unchanged condition.

By this theory the whole question is resolved into one of surface attraction, and the action is said to be identical with that which takes place when a weak solution of the same colouring matter is decolorised by filtering through animal charcoal.

On the whole, the mechanical theory of dyeing seems to have most points in its favour, although it cannot be denied that an alteration in the chemical composition of a fibre may materially alter its behaviour towards certain colouring matters. The most striking example of this kind is that exhibited by cotton, when changed into oxycellulose through the action of hypochlorous acid (*see* p. 11).

91. Pigments and Colouring Principles.—To return now to the second of the two essential elements dealt with by the dyer, namely, the colouring matter; so excessively varied are the bodies belonging to this class, both in physical and chemical properties, that it is again not at all surprising that they should behave differently, even towards the same fibre.

If two pieces of wool are treated in separate vessels, the one with a solution of Magenta and the other with Alizarin, the former will soon be dyed red, while the latter only assumes a brownish-yellow stain of no practical use.

If a third piece of wool is first heated in a solution containing a suitable amount of aluminium sulphate and cream of tartar, and, after washing well, is then boiled with Alizarin and water (preferably somewhat calcareous), it acquires a bright red colour.

When other metallic salts—*e.g.*, potassium dichromate, stannous chloride, ferrous sulphate, &c.—are substituted for the aluminium sulphate, the wool becomes dyed other colours, namely, claret-brown, orange, purple, &c.

If similar experiments are made with Magenta, the wool always assumes a more or less similar magenta-red tint.

It is quite evident from these experiments that Magenta and Alizarin have totally different dyeing properties; they are indeed typical representatives of two distinct classes of colouring matters.

The members of the one class are *coloured bodies* or *pigments* in which the colour is fully developed, and they require simply to be fixed on the textile fibre, more or less in their unchanged state, to cause the latter to become dyed. Such colouring matters may be conveniently termed *monogenetic*, since they are only capable of yielding, at most, various shades of *one* colour. To this class belong Magenta, Indigo, Orceïn (orchil), Picric Acid, Methyl Green, &c. The members of this class may be soluble (Magenta), or insoluble (Aniline Black), organic (Indigo), or inorganic (Ultramarine Blue).

As to the members of the other class of colouring matters, although they are generally possessed of some colour, this is not an essential feature, and even when present it generally lacks intensity, and does not necessarily bear the slightest relationship to the colours obtainable from them in dyeing. As a rule, they are to be considered as *colouring principles* capable of yielding several colours, *i.e.*, very distinct coloured bodies, according to the means employed for the production of the latter, and hence an appropriate name for them may be *polygenetic* colouring matters. To this class belong Hæmateïn (logwood), Alizarin (madder), Galleïn, &c.

From what has just been stated, it will be understood that the general mode of applying the members of these two classes of colouring matters in dyeing is very different. This is, however, only partially true, for the distinction between monogenetic and polygenetic colouring matters in this respect is not sharply defined, since there are those which stand, as it were, on the border-land between the two. Some of the monogenetic colouring matters—*e.g.*, Alizarin Blue, Cœruleïn, &c.—combine the properties of colouring principles and of veritable pigments. The method of applying them to the textile fibres is that usual with the polygenetic class, but they are only capable of yielding various tones of one colour, and they can also be applied by special methods adopted with certain monogenetic colouring matters, for instance, Indigo.

The presence of the fibre in the third experiment cited above, is not a condition essential to the development of the colour, as can be readily enough shown by the following experiment:—Make a dilute solution of aluminium sulphate, and render it somewhat basic and more sensitive by neutralising a portion of its sulphuric acid with sodium carbonate; add now to the still clear solution a little alizarin, and shake the mixture vigorously, or heat it a little. A red-coloured body is very soon produced in the form of an insoluble precipitate, especially if a calcium salt be also present. It would appear in this case that the colouring matter enters into chemical combination with the aluminium, or with a very basic salt of the same.

Analogous but variously-coloured precipitates are produced on substituting decoctions of Cochineal, Persian berries, Logwood, &c., for the Alizarin, or by replacing the aluminium sulphate with solutions of other metallic salts. Coloured precipitates produced in this manner are the real colours or pigments which it is desired to obtain from the polygenetic colouring matters; indeed, when dried, ground, and mixed, say, with boiled oil, they are used by the painter under the name of *lakes.* The object of the dyer, however, is not only to produce, but, at the same time, to fix these coloured precipitates or lakes on the material to be dyed, without the aid of such a vehicle as boiled oil.

To effect this, two operations as a rule are necessary, namely, *mordanting* and *dyeing.*

92. The Mordanting Process.—The first has for its object, the precipitation and fixing upon the textile material as firmly and permanently as possible, of some substance capable of combining with the colouring matter subsequently to be applied, and precipitating it in an insoluble state upon the fibre. This operation or series of operations constitutes the *mordanting* process, and the metallic salts or other substances used for this purpose are termed *mordants.* This name is derived from the Latin, *mordere*, to bite. It was originally introduced because the early French dyers considered that the utility of these metallic salts consisted in their corrosive nature; the general opinion was that they simply made the textile fibres rough, that they opened their pores, and thus rendered them more suitable for the entrance of the colouring matters. No doubt some slight corrosive action does take place here and there, in which case, of course, the surface of the fibres will be increased, entailing, probably, a slight increase of physical attraction of the fibre for colouring matters, but the essential action of mordants is undoubtedly chemical. As to the manner of applying these mordants, it varies with the different origin and state of manufacture of the textile fibres, the nature of the mordants and colouring matters employed, the particular effects to be obtained, and so on.

The method generally adopted in the case of the *woollen fibre* is to boil it with dilute solutions of the metallic salts, frequently with the addition of acid salts, *e.g.*, cream of tartar, &c. A partial dissociation of the metallic salts takes place, induced and augmented both by the dilution and heating of the solution and the addition of assistant acids and salts, and partly by the presence of the fibre itself. What actually becomes fixed upon the fibre during this process is in most cases more or less a matter of conjecture, the chemistry of the process having been as yet only imperfectly studied.

Although the term mordant is generally applied only to the metallic salts used, a mordant in the widest sense of the term is that body, whatever it may be, which is fixed on the fibre in combination with any given colouring matter. In the case cited of dyeing wool alizarin-red, it is considered that during the boiling of the wool with cream of tartar and aluminium sulphate, this latter salt is decomposed, and the mordant precipitated on the fibre is insoluble alumina, or a basic aluminium sulphate; in the subsequent dye-bath this combines with the alizarin to produce the red-coloured compound, or lake.

Silk and wool have many analogous properties, and hence the *silk fibre* is frequently mordanted in a manner similar to that employed for wool, but as a rule high temperatures are avoided, and mere immersion in a cold concentrated metallic salt solution, with a subsequent washing with water, is all that is necessary. During the immersion the silk absorbs the metallic salt more or less unchanged, but in the subsequent washing, this absorbed salt is dissociated by the mere dilution with water, and an insoluble basic salt is precipitated within the substance of the fibre. Certain soluble basic ferric sulphates, basic aluminium sulphates, and stannic chloride, behave in this manner.

As to the methods employed for mordanting *cotton*, they are usually more complex, since this fibre has not the property, like silk and wool, of decomposing metallic salts by such a simple method as boiling in their solutions, nor is it so porous as these fibres. In some cases, metallic salts are chosen whose component parts are, under certain conditions, readily separable from each other, such as acetates of iron and aluminium, and with these, after immersing the cotton in their solutions, and removing the excess, it may suffice to dry the cotton and then to expose it for some time to air rendered suitably warm and moist ("ageing").

Ferrous acetate absorbs oxygen from the air most energetically, and forms already in this way a difficultly soluble basic salt.

$$\underset{\text{Ferrous acetate.}}{2[Fe(C_2H_3O_2)_2]} + O + H_2O = \underset{\text{Basic ferric acetate.}}{Fe_2(C_2H_3O_2)_4(OH)_2}$$

In most cases of mordanting, however, whether the material be silk, wool, or cotton, there is precipitated upon the fibre a metallic oxide, or a basic metallic salt, with a corresponding liberation of acid, or formation of an acid salt, and the mordanting process continues only as long as the constantly increasing acid allows, *i.e.*, until a state of equilibrium proper to the new conditions has become established.

The advantage of using the metallic acetates as mordants for cotton is, that the liberated acid does not injure or tender the fibre, which is readily the case with other salts; further, owing to its volatility, the acetic acid is quickly removed, under suitable conditions of heat and moisture, from the field of action, and a more perfect precipitation of the real mordanting body on the fibre takes place.

In some cases of mordanting cotton, the use of acetates, and the simple exposure or "ageing" referred to, are avoided, either from motives of economy or because certain practical difficulties arise. With cotton *yarn*, for example, the drying is apt not to be uniform, and irregular colours result from unequal decomposition of the acetate. Even where acetates are both applicable and preferable, it is not always the case that the "ageing" process causes the maximum amount of mordant to be fixed upon the fibre. In such cases, other modes of getting rid of the acid are adopted, and other mordanting salts even are employed. The mordanting base may be fixed upon the fibre by using a weak alkaline bath of ammonia, chalk, sodium carbonate, &c., or by using such alkaline salts as not only remove the acid, but also produce insoluble compounds with the base, *e.g.*, sodium silicate, phosphate, arsenate, &c. This method is adopted by the calico-printer in the operation of "cleansing" or "dunging," which succeeds the "ageing" and precedes the dyeing operations.

When the mordanting body is applied in alkaline solution, *e.g.*, stannic oxide, as stannate of soda, a slightly acid bath (sulphuric acid) is required for its precipitation upon the fibre. This is a method also frequently used by the calico-printer.

Still another method of fixing the mordant on textile fabrics is that of *steaming*, a process adopted for certain styles of work by the printer of cotton, wool, and silk materials.

In the calico styles referred to, a mixture of polygenetic colouring matter (*e.g.*, Alizarin) and metallic salt (*e.g.*, aluminium acetate) is printed upon the fabric, which is then dried and submitted to the action of steam in a closed box. During this steaming process, the metallic salt employed as mordant is decomposed, a greater or less proportion of its acid is driven off, and the remaining oxide or basic salt is fixed upon the fibre. Not only so, however, but, at the high temperature employed, combination between the colouring matter and mordant takes place, coloured pigment is produced, and is at the same time firmly fixed upon the fibre.

The mordanting and dyeing operations are combined in an analogous manner when applying certain colouring matters to wool by dyeing, since this fibre possesses the property of decomposing acid solutions of colour-lakes, and even of attracting and mechanically fixing the latter when undissolved, if sufficiently finely divided.

93. Colour-Acids and Colour-Bases.—In the above cases, where polygenetic colouring matters are employed, the actual mordants fixed on the textile fibre have more or less a basic character; as already stated, they are metallic oxides or basic metallic salts, and although these colouring matters are not really acids, but rather bodies of an alcoholic or phenolic nature, they possess so much of the acid character, that they combine with these and other bases; it is not at all improbable indeed that the colouring matter and the mordant (when this is necessary) must always bear some such definite relationship towards each other. All polygenetic colouring matters known hitherto possess the acid character referred to.

It has been stated that cotton does not become permanently dyed when immersed in a hot solution of Indigo Extract or of Magenta. In so far as this latter colouring matter is a red-coloured body, although soluble, it may be considered analogous to the alizarin-red pigment produced by the combination of alumina and Alizarin. The question arises, is it similarly constituted? is it produced by the combination of a basic body with one of an acid character? Experiment answers yes, and shows it to be a chemical compound of a colourless base rosaniline with hydrochloric acid. It does seem, therefore, to have a constitution somewhat analogous to that of alizarin-red, but of a reverse character. In Magenta, the colouring power resides in the basic part of the compound (rosaniline), whereas in the alizarin-red it is to be found in the acid portion (Alizarin), although in each case the other constituent is equally necessary to the production of a coloured body. Such considerations lead one to distinguish *colour-acids* and *colour-bases*, and we may infer that if the former, as we have seen, require basic mordants, the latter will probably require acid mordants. Among the numerous monogenetic colouring matters, there is an extensive class of colour-acids which differ considerably in chemical constitution from those which possess an alcoholic or phenolic character like Alizarin. They contain the atomic group (HSO_3), are analogous more or less to acid sulphites, and have been termed 'sulphonic acids." To this class belong Indigo Extract, Croceïn Scarlet, &c. Some colouring matters, *e.g.*, Indigotin, may be regarded as of a neutral or indifferent character.

In endeavouring to fix Magenta upon cotton, the question arises, will the colourless rosaniline combine with any other acid than hydrochloric acid to form an insoluble red or otherwise coloured compound? Is it capable of forming a lake? If so, the next question is, is the requisite acid capable of being fixed upon cotton in such a manner that it can still combine with the rosaniline? Experiment shows that there are such acids, *e.g.*, tannic acid. If a solution of Magenta is mixed with a solution of tannic acid (either free or neutralised with an alkali), an insoluble red-coloured tannate of rosaniline will be precipitated. Cotton has a natural attraction for tannic acid, so that when once steeped in its solutions it is not readily removed by washing. In order to dye cotton, therefore, with Magenta, it suffices to immerse it for some time in a solution of tannic acid, and after drying, to pass it into a solution of Magenta. The red tannate of rosaniline thus produced upon the fibre does not, however, possess the character of absolute insolubility, especially in alkaline and soapy liquids, so that the dye cannot be considered entirely satisfactory. But, just as it has been seen that certain alkali salts can be used for the better fixing of the basic mordants on cotton, by reason of their *acid*, so here certain metallic salts can be used to fix such acid mordants as tannic acid, but in this case by reason of their *base*.

In applying Magenta to cotton, for example, a dye much faster to boiling soap solutions is obtained, if the tannic acid prepared cotton is passed into a solution of an antimony or tin salt—*e.g.*, tartar emetic, or stannic chloride—previous to its immersion in the solution of Magenta. By this means the tannic acid is fixed upon the cotton in a very insoluble form, as tannate of antimony or tin.

Acid mordants, which act in the same manner as tannic acid, and fix the basic colouring matters upon cotton, are not numerous, but oleïc acid and other fatty acids may be mentioned as such. It is interesting to note that colouring matters of an acid character (*e.g.*, Alizarin) when fixed on cotton, may also behave as mordants towards basic colouring matters. Alizarin purples and alizarin reds on cotton can be readily dyed with Methyl Violet, Magenta, &c. Hitherto, all the acid mordants employed to fix any particular basic colouring matter on textile fabrics have produced only similar shades of colour. Basic colouring matters are hence all monogenetic.

Since, however, both oleïc and tannic acid can combine not only with *organic* colour-bases in the manner just described, but also with certain metallic oxides (*inorganic* bases), to produce insoluble compounds, they may be, and are, indeed, employed as fixing agents for the latter in the same way as the alkaline phosphates, arsenates, &c.

A usual method of dyeing cotton black, for example, is first to impregnate the cotton with a solution of tannic acid (decoction of sumach, &c.), and afterwards with a solution of a ferric salt (nitrate of iron).

The mordant (ferric oxide) is in this way fixed on the cotton by means of the tannic acid. Thus mordanted, the cotton is ready to be dyed in a decoction of logwood.

Another notable example of the same kind is afforded by the method employed in dyeing Turkey-red. Here the cotton is first impregnated with oleïc acid, or other oil compound of similar character, and is afterwards immersed in a solution of an aluminium salt. The mordant alumina is fixed on the cotton by means of the oil compound, and yet it combines with the alizarin in the subsequent dye-bath, to produce the red pigment.

Apart from this preliminary precipitation and fixing of the basic or acid mordant on the cotton previous to the application of a colour-acid or colour-base, the fixing of all colouring matters upon cotton seems to depend largely on their capability of forming insoluble precipitates or lakes.

Colouring matters, like Indigo Extract, Croceïn Scarlet, &c., which do not form any sufficiently insoluble compound with bases, are not suitable for dyeing cotton.

In dyeing with Indigo and Safflower, the colouring matters are themselves readily precipitated from their solutions, either by oxidising or acid influences.

With Turmeric, and some few other dye-stuffs, precipitation is not necessary, since cotton is dyed with these by merely steeping it in their decoctions, and the case seems to be analogous to the dyeing of wool with Magenta.

MORDANTS.

CHAPTER XI.

USE OF MORDANTS.

94. Application of Mordants.—In the opening words of the preceding chapter it was stated that the two most essential elements in the operations of the dyer are, the material to be dyed, and the colouring matter to be applied; but from what has been said, it is evident that the mordant plays an almost equally important part, according to the particular colouring matter and fibre dealt with.

Whenever mordants are necessary, the method of application should not perceptibly affect the physical characteristics of the fibre—for example, its strength, elasticity, feel, lustre, &c.—and the ultimate colour produced should be as bright as possible. It is important that sufficient time and suitable conditions be allowed for the mordant solution to penetrate the fibre thoroughly, and that the change of the mordant from the soluble to the insoluble state should not be too rapid. If the mordant is merely fixed on the fibre superficially, the dyes eventually produced are not "fast," especially to rubbing, and are totally devoid of brilliancy or bloom. The chemically different nature of each individual colouring matter and mordant, and the different behaviour of the several textile fibres, compel us to determine the best method of fixing for each colouring matter and mordant.

And although one may make use of class relationships, and there may be certain broad lines to work upon, the time has not arrived for laying down any theory of the fixing of mordants or colouring matters which shall be generally applicable and satisfactory.

In the following pages, the most important mordants in use at the present time will be considered; the outlines of their manufacture will be given; and special though brief reference to their chemical behaviour under practical conditions will be made.

ALUMINIUM MORDANTS.

These are perhaps the most generally important of all mordants. They have been employed from time immemorial, and are at present used for all fibres.

95. Aluminium Sulphate [$Al_2(SO_4)_3 \cdot 18H_2O$].—This normal salt is known also in a more or less pure state as "cake-alum," "concentrated alum," and "patent alum." It is prepared by dissolving alumina in sulphuric acid, and evaporating the solution until it solidifies on cooling. The chief difficulty in its manufacture is to obtain an alumina sufficiently free from iron. This requisite is now obtained as a by-product in the manufacture of sodium carbonate from cryolite. Another source is the mineral bauxite, which consists essentially of alumina, with a slight admixture of ferric oxide, and frequently also of silica.

At the present time very pure normal aluminium sulphate appears as an article of commerce in the form of irregular lumps, having a fused appearance; it may serve very conveniently for the preparation of all other aluminium mordants.

If a solution of the normal salt be neutralised to a greater or less degree—*e.g.*, by the addition of mono- or di-sodium carbonate, chalk, aluminium hydrate, &c.—solutions of so-called *basic aluminium sulphates* are obtained. These vary in composition according to the extent of the neutralisation, as shown by the following equations :—

$$\underset{\substack{\text{Normal}\\ \text{aluminium sulphate.}}}{Al_2(SO_4)_3\cdot18H_2O} + \underset{\substack{\text{Monosodium}\\ \text{Carbonate.}}}{2NaHCO_3} = \underset{\substack{\text{Basic}\\ \text{aluminium sulphate.}}}{Al_2(SO_4)_2(OH)_2} + \underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Carbonic}\\ \text{acid.}}}{2CO_2} + \underset{\text{Water.}}{18H_2O}$$

$$2[Al_2(SO_4)_3\cdot18H_2O]+6NaHCO_3 = \underset{\substack{\text{Basic}\\ \text{aluminium sulphate.}}}{Al_4(SO_4)_3(OH)_6} + 3Na_2SO_4 + 6CO_2 + 36H_2O$$

$$Al_2(SO_4)_3\cdot18H_2O + 4NaHCO_3 = \underset{\substack{\text{Basic}\\ \text{aluminium sulphate.}}}{Al_2(SO_4)(OH)_4} + 2Na_2SO_4 + 4CO_2 + 18H_2O$$

Numerous experiments by Liechti and Suida have shown that the more basic the solution the more readily is it dissociated, either on heating or on diluting with water, and the greater is the proportion of alumina fixed on the cotton fibre by steeping and afterwards drying at a low temperature. Whereas, for example, a solution of normal aluminium sulphate (200 grams per litre) gives no precipitate, either by boiling or when diluted with water, and gives up to the cotton fibre only about 13 per cent. of the alumina presented to it, an equivalent solution of the basic salt $Al_4(SO_4)_3(OH)_6$ begins to be precipitated when heated to 68° C., or when diluted with twice its volume of cold water, and gives up to the cotton fibre 58·7 per cent. of the available alumina. A solution of $Al_2(SO_4)_2(OH)_2$, which is perhaps the most usually employed of the basic sulphates, holds in the above respects an intermediate position, since it is precipitated only after boiling for half an hour, or by diluting with water fourteen-fold, and it yields under similar conditions 51 per cent. Al_2O_3 to the cotton fibre The dissociation is always accelerated by the presence of sodium sulphate in the solution, and in the case of

$Al_2(SO_4)_2(OH)_2$ its presence causes the precipitate produced by boiling to re-dissolve on cooling.

When solutions of basic aluminium sulphates are boiled, a still more basic and insoluble salt is precipitated, especially in the presence of the textile fibres, and a normal or even acid salt remains in solution. Similar changes evidently occur when the fibres impregnated with the solutions are dried, and it is on these facts that the use of basic salts in mordanting depends.

Good normal aluminium sulphate is more economical as a basis for the manufacture of other aluminium mordants than its double salts, the alums of commerce, so usually employed. It contains a larger percentage of the useful constituent alumina (15 per cent.), and none of the comparatively useless and expensive ammonium or potassium sulphate. Till recently, the alums have been preferred because they are more regular in composition, and less liable to contain iron, but these defects are not necessarily met with in aluminium sulphate at the present time.

The presence of iron, which must be at all times strenuously avoided, is readily detected by noticing the characteristic (black or blue) colorations, or precipitates, produced by adding to a concentrated solution of the aluminium sulphate one or other of the following solutions, tannic acid, logwood liquor, a mixture of potassium ferro- and ferri-cyanide. It is well to bear in mind that the iron may be present either as a ferrous or a ferric salt.

Application of Aluminium Sulphate to the several Fibres.

96. *Application to Cotton.*—Owing to the great stability of normal aluminium sulphate, this is by no means a useful mordant when employed alone. If cotton is boiled with its solution, no precipitation of insoluble basic salt, and hence no mordanting, takes place. Even under the more favourable mode of impregnating the

cotton with its solution and drying, its mordanting power is, as already indicated, comparatively feeble. Very much better results are obtained by this so-called *ageing* method when *basic* aluminium sulphate is used. But the method is not employed in practice even then, because of the liability of the fibre to become tendered by the acid, or acid salt which is liberated, and because with loose-cotton, or cotton-yarn, it would certainly give irregular results through unequal drying, and, consequently, unequal decomposition of the mordant.

The preferable method is that of *precipitation*, in which, after impregnating the fibre evenly with basic aluminium sulphate, the material is dried and passed into a solution of some salt capable of fixing the alumina on the fibre, either by precipitating it as such, or combining with it to produce an insoluble compound. The following substances may be used for this purpose; ammonium carbonate, ammonia, phosphate of soda, arsenate of soda, silicate of soda, soap, ammoniacal sulphated oil, &c.

The choice of fixing agent should be determined by experiment, since the state in which the alumina is fixed upon the fibre influences considerably the ultimate result, both as to brilliancy of colour and fastness. To obtain the best result, the choice may vary with each colouring matter employed. The concentration and temperature of the fixing solution, and the duration of immersion, should also, in each case, be accurately determined. The following must be taken, therefore, only as an approximate guide for further experiments.

Prepare the following solution of basic aluminium sulphate: one litre of water, 200 grams of normal aluminium sulphate, 31·82 grams of di-sodium carbonate, Na_2CO_3; make the solution to stand at 10° Tw. (Sp. Gr. 1·05).

Impregnate the cotton with this solution, remove excess of liquid by squeezing or wringing, dry at a low temperature, and pass into cold water containing fifty grams of strong commercial ammonia liquor (0·88 Sp. Gr.)

per litre. After working the cotton in this solution for five or ten minutes, and washing well, it is ready for dyeing.

If soap be the fixing agent employed, make a solution containing ten grams per litre.

If arsenate or phosphate of soda, use from five to ten grams per litre.

If silicate of soda at 100° Tw. (Sp. Gr. 1·5) use five to ten grams per litre.

When sulphated oil is employed, it is best to impregnate the cotton with a solution of this first, and pass afterwards into the solution of basic aluminium sulphate.

The amount of alumina precipitated upon the fibre in this case is determined by the concentration of the sulphated oil solution employed, and not by that of the aluminium salt solution.

Impregnate the cotton thoroughly with an aqueous solution containing 50—150 grams of sulphated oil per litre, remove the excess of liquid by squeezing or wringing, and dry in a stove. The cotton is then worked for a short time, or steeped in a solution of basic aluminium sulphate at 10° Tw. (Sp. Gr. 1·05), and finally washed with water.

Tannic acid is sometimes employed in the same manner as sulphated oil.

97. *Application to Wool.*—In mordanting wool, the normal aluminium sulphate is to be preferred to the basic salt, since the latter is too sensitive. Under the conditions necessary to be imposed, it would be apt to decompose too rapidly, the wool would be more or less superficially mordanted, and the ultimate colour would be dull, and liable to rub off; moreover, the wool would acquire an unpleasant, harsh feel.

Simple steeping of the wool in a cold aluminium sulphate solution, even with subsequent drying, gives an unsatisfactory result.

In order to expel the air from within and around the wool fibre, and also to soften the latter, and thus render it thoroughly permeable, it is necessary that a boiling solution be employed.

In most cases the addition to the solution of a certain proportion of bi-tartrate of potash is found extremely beneficial, since it adds depth and brilliancy to the ultimate colour. (*See* Alizarin, p. 454). This addition evidently causes an increased amount of alumina to be precipitated upon the fibre. In some cases, however (*see* Old Fustic and other Yellow Dyewoods, p. 360), it renders the ultimate colour dull.

To mordant wool efficiently with aluminium sulphate, prepare the following solution: one litre of water, eight grams of aluminium sulphate, seven grams of bi-tartrate of potash (cream of tartar). Immerse the wool in the cold solution, raise the temperature gradually to the boiling point in the course of 1—1½ hours, and continue boiling half an hour longer, then wash well.

98. *Application to Silk.*—Up to the present time, aluminium sulphate does not seem to be generally used in mordanting silk, the older and better-known alum being employed instead. It is very probable, however, that the normal aluminium sulphate could be substituted with advantage in most cases.

The method to be adopted is as follows:—Wet out the silk thoroughly with water, remove excess, then work it about for a little in a strong solution of the aluminium salt, and steep for several hours, or over-night. Finally, wash well with water, preferably somewhat calcareous.

During the steeping process the silk simply absorbs the solution, or, at any rate, the fixing of alumina takes place only to a slight extent; but during the subsequent washing, the absorbed salt is more or less completely dissociated. This is particularly the case when *basic* aluminium sulphate has been employed, the result being, that a *still more basic* and *insoluble* salt remains permeating the substance of the fibre.

The wetting of the silk before steeping in the mordant solution is essential in order to insure a more rapid and even absorption of the solution.

When the mordanting of the silk precedes the dyeing operation, the aluminium sulphate bath can be retained as a permanent one, in which case its concentration simply requires to be kept constant by occasionally making further additions of aluminium sulphate; but when the bath must be used between other operations, it may become necessary to throw away the solution each time.

Silk mordanted with aluminium sulphate should not be allowed to dry while still impregnated with the solution, otherwise it acquires an unpleasant feel, and is difficult to wet afterwards.

99. Alum.—Two kinds of alum may be met with in commerce, viz., *ammonia alum* $\left.\begin{matrix}(NH_4)_2\\ Al_2\end{matrix}\right\}(SO_4)_4 \cdot 24\,H_2O$, and *potash alum* $\left.\begin{matrix}K_2\\ Al_2\end{matrix}\right\}(SO_4)_4 \cdot 24H_2O$. The first contains 11·9 per cent. Al_2O_3, the second 10·83 per cent. Although they contain less of this mordanting principle than aluminium sulphate, they are perhaps, even now, more largely used by dyers than the latter, since they bear the seal of regular composition in their crystalline state.

They are prepared from aluminous shale. This is burnt or roasted, then dissolved in sulphuric acid, and ammonia or potassium sulphate is added to the solution; the respective alums thus formed are separated from the iron, which is always present, by repeated crystallisation and washing.

The best qualities of alum are in the form of large glassy-looking crystals, and are entirely free from iron.

By the addition of caustic alkali, alkaline carbonates, &c., to normal alum solutions, so-called "neutral" and "basic" alums are produced, which are analogous to the basic aluminium sulphates already spoken of, and their solutions, when heated or diluted, are dissociated and produce precipitates in a similar manner. If a solution of alum, rendered by addition of sodium carbonate as basic as it can be made without precipitation, is allowed to evaporate slowly at the ordinary temperature, a crystalline crust is deposited, which contains the basic salt $Al_4(SO_4)_3(OH)_6$ and potassium sulphate. If the solution is heated above 40° C. a precipitate supposed to consist of $\left.\begin{matrix}K_2\\ Al_2\end{matrix}\right\}(SO_4)_2(OH)_4$ is produced.

The alums are applied as mordants to the various fibres in the same way as aluminium sulphate.

100. Aluminium Acetates.—A solution of normal aluminium acetate $Al_2(C_2H_3O_2)_6$ may be prepared either by dissolving aluminium hydrate in acetic acid, or by adding a solution of lead acetate to a solution of normal aluminium sulphate, in the proportions indicated by the following equation :—

$$\underset{\text{Aluminium sulphate.}}{[Al_2(SO_4)_3\cdot 18H_2O]} + \underset{\text{Lead acetate.}}{3[Pb(C_2H_3O_2)_2\cdot 3H_2O]} = \underset{\text{Aluminium acetate.}}{Al_2(C_2H_3O_2)_6} + \underset{\text{Lead sulphate.}}{3PbSO_4} + \underset{\text{Water.}}{27H_2O}$$

On carefully evaporating a solution of the normal acetate (which always smells of acetic acid), to dryness at a low temperature, a gummy mass having the composition $Al_2(C_2H_3O_2)_4(OH)_2$ is obtained. This does not smell of acetic acid, and it has hence been considered by Crum as the normal salt, and that in the solution there is free acetic acid present.

By adding to a solution of the normal salt increasing amounts of an alkaline carbonate, solutions of various basic aluminium acetates are formed, as shown by the following equations :—

$$\underset{\substack{\text{Normal}\\ \text{aluminium acetate.}}}{Al_2(C_2H_3O_2)_6} + \underset{\substack{\text{Monosodium}\\ \text{carbonate.}}}{NaHCO_3} = \underset{\substack{\text{Basic}\\ \text{aluminium acetate.}}}{Al_2(C_2H_3O_2)_5(OH)} + \underset{\substack{\text{Sodium}\\ \text{acetate.}}}{Na(C_2H_3O_2)} + \underset{\substack{\text{Carbonic}\\ \text{acid.}}}{CO_2}$$

$$Al_2(C_2H_3O_2)_6 + 2NaHCO_3 = \underset{\text{Basic aluminium acetate.}}{Al_2(C_2H_3O_2)_4(OH)_2} + 2Na(C_2H_3O_2) + 2CO_2$$

$$Al_2(C_2H_3O_2)_6 + 3NaHCO_3 = \underset{\text{Basic aluminium acetate.}}{Al_2(C_2H_3O_2)_3(OH)_3} + 3Na(C_2H_3O_2) + 3CO_2$$

$$Al_2(C_2H_3O_2)_6 + 4NaHCO_3 = \underset{\text{Basic aluminium acetate.}}{Al_2(C_2H_3O_2)_2(OH)_4} + 4Na(C_2H_3O_2) + 4CO_2$$

Solutions of these various basic acetates *containing sodium acetate* are precipitated on heating, and the more basic they are the lower is the temperature at which dissociation (precipitation) takes place, but, strange to say, the more dilute the solution the higher the temperature of dissociation. By mere dilution with water they are not precipitated. (Liechti and Suida.)

Solutions of freshly prepared *pure* normal aluminium acetate (equivalent to 200 grams per litre of the normal sulphate) are not precipitated either by heating or by dilution, but on standing for a length of time, they decompose spontaneously with deposition of alumina, especially, it is said, when exposed to light.

Solutions of all aluminium acetates (normal and basic) are precipitated both by heating and by dilution, *if they contain sulphates, e.g.*, K_2SO_4, $Al_2(SO_4)_3$, &c., and this is always the case with those basic acetates manufactured from aluminium sulphate when a portion of the lead acetate has been replaced by alkaline carbonates, thus :—

$$\underset{\substack{\text{Aluminium}\\\text{sulphate.}}}{Al_2(SO_4)_3 \cdot 18H_2O} + \underset{\substack{\text{Disodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Lead acetate.}}{2[Pb(C_2H_3O_2)_2 \cdot 3H_2O]} =$$

$$= \underset{\substack{\text{Basic}\\\text{aluminium acetate.}}}{Al_2(C_2H_3O_2)_4(OH)_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Lead}\\\text{sulphate.}}}{2PbSO_4} + \underset{\substack{\text{Carbonic}\\\text{acid.}}}{CO_2} + \underset{\text{Water.}}{24H_2O}$$

It matters not whether the sodium carbonate is added before or after the lead acetate, the final result is the same.

It also matters little at what stage the alkaline carbonate be added for the production of a basic acetate, whenever the amount of lead acetate employed is sufficient to precipitate the whole of the sulphuric acid of the aluminium sulphate, but in this case there is not alkali *sulphate,* but always *acetate* in the solution, thus :—

$$\underset{\substack{\text{Aluminium}\\\text{sulphate.}}}{Al_2(SO_4)_3 \cdot 18H_2O} + \underset{\substack{\text{Disodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\text{Lead acetate.}}{3[Pb\,(C_2H_3O_2)_2 \cdot 3H_2O]} =$$

$$\underset{\substack{\text{Basic}\\\text{aluminium acetate.}}}{Al_2(C_2H_3O_2)_4(OH)_2} + \underset{\substack{\text{Sodium}\\\text{acetate.}}}{2Na(C_2H_3O_2)} + \underset{\substack{\text{Lead}\\\text{sulphate.}}}{3PbSO_4} + \underset{\substack{\text{Carbonic}\\\text{acid.}}}{CO_2} + \underset{\text{Water.}}{27H_2O}$$

When a solution of normal aluminium acetate containing sulphates is precipitated by heating, the precipitate re-dissolves on cooling, but this does not take place with the basic acetates under any circumstances. The precipitate thus produced in the presence of sulphates has been considered by some to be simply aluminium hydrate, but careful analysis has shown that it contains a small amount of sulphuric acid ; in other words, it is an exceedingly basic aluminium sulphate.

Experiments by Liechti and Suida have shown that if cotton be impregnated with a solution of normal aluminium acetate (equivalent to 200 grams of normal sulphate per litre), then dried at a low temperature, about 50 per cent. of the available alumina is fixed on the fibre, whereas an equivalent solution of the basic salt $Al_2(C_2H_3O_2)_4(OH)_2$ containing Na_2SO_4 yields, under the same conditions, nearly the whole of its alumina to the fibre.

Aluminium acetates (especially the normal salt) prepared by means of lead acetate, are liable to contain a certain amount of lead sulphate, since this is soluble in aluminium acetate; hence, in cases where such contamination would be injurious—*e.g.*, in steam-alizarin-reds for calico-printing—the lead acetate may be advantageously replaced by an equivalent amount of calcium or barium acetate. The solubility of lead sulphate is lessened, however, by the presence of soluble sulphates, so that where a large excess of aluminium sulphate is present through a limited use of lead acetate, only traces of lead sulphate are found in the solution, and solutions of *basic* acetates, in the preparation of which a suitable amount of sodium carbonate has replaced some of the lead acetate, may be entirely free from lead.

101. Aluminium Sulphate-Acetates. — It has long been known that there is no practical advantage in employing an amount of lead acetate sufficient to decompose the whole of the aluminium sulphate. D. Köchlin explains this by stating that the real mordanting body fixed on the fibre is not necessarily pure aluminium hydrate, but may be, and in most cases probably is, an insoluble basic aluminium sulphate. He finds it possible, indeed, to prepare an excellent mordanting solution by dissolving insoluble basic aluminium sulphate in warm acetic acid. A precipitate of the necessary basic sulphate is obtained by carefully neutralising a solution of alum with sodium carbonate until the precipitate at first formed just ceases to re-dissolve, and then boiling the solution.

D. Köchlin's solution and those prepared from aluminium sulphate by using a deficiency of lead acetate, contain so-called *aluminium sulphate acetates*. Their mode of formation is illustrated by the following equations :—

$$\underset{\text{Aluminium sulphate.}}{Al_2(SO_4)_3\cdot18H_2O} + \underset{\text{Lead acetate.}}{2[Pb(C_2H_3O_2)_2\cdot3H_2O]} =$$

$$= \underset{\text{Aluminium sulphate-acetate.}}{Al_2SO_4(C_2H_3O_2)_4} + \underset{\text{Lead sulphate.}}{2PbSO_4} + \underset{\text{Water.}}{24H_2O}$$

$$2[Al_2(SO_4)_3\cdot18H_2O] + 3[Pb(C_2H_3O_2)_2\cdot3H_2O] + \underset{\text{Monosodium carbonate.}}{2NaHCO_3} =$$

$$= \underset{\text{Basic aluminium sulphate-acetate.}}{2[Al_2SO_4(C_2H_3O_2)_3OH]} + \underset{\text{Lead sulphate.}}{3PbSO_4} + \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Carbonic acid.}}{2CO_2} + \underset{\text{Water.}}{45H_2O}$$

$$Al_2(SO_4)_3\cdot 18H_2O + Pb(C_2H_3O_2)_2\cdot 3H_2O + 2NaHCO_3 =$$

$$= \underset{\substack{\text{Basic aluminium}\\ \text{sulphate-acetate.}}}{Al_2SO_4(C_2H_3O_2)_2(OH)_2} + PbSO_4 + Na_2SO_4 + 2CO_2 + 21H_2O$$

$$Al_2(SO_4)_3\cdot 18H_2O + \underset{\text{Acetic acid.}}{C_2H_4O_2} + 4NaHCO_3 =$$

$$= \underset{\substack{\text{Basic aluminium}\\ \text{sulphate-acetate.}}}{Al_2SO_4(C_2H_3O_2)(OH)_3} + 2Na_2SO_4 + 4CO_2 + 19H_2O$$

Experiments by Liechti and Suida have shown that increase of basicity in the aluminium sulphate-acetates lowers their dissociation point, both on heating and diluting with water, *i.e.*, the sensibility of their solutions is increased. In all cases, the precipitate produced by heating is gelatinous, and if the sulphate-acetate is not more basic than $Al_2SO_4(C_2H_3O_2)_3(OH)$, the precipitate is almost entirely re-dissolved on cooling.

The aluminium sulphate-acetates yield nearly the whole of their alumina to the cotton fibre during impregnation and drying, and act, therefore, in this respect much stronger than the aluminium sulphates, and about the same as the basic aluminium acetate $Al_2(C_2H_3O_2)_4(OH)_2$.

The technical name given to solutions of the various aluminium acetates and sulphate-acetates used in practice, is *red liquor*, because they are universally employed by the calico-printer and cotton-dyer as the mordant for producing alizarin reds.

Considerable licence is apparently taken in practice in the manufacture of "red liquors" required for different purposes and styles of work, both with regard to the particular ingredients used, and their relative proportions. Apart from the fact that their real value is determined by practical results, the above considerations show that numerous variations in composition are possible, which cause them to behave very differently.

The following may be taken as representative of the innumerable recipes adopted in the manufacture of various red liquors :—

	gms.	gms.	gms.	gms.	gms.	gms.	gms.	gms.	gms.	gms.
Water . . .	250	300	400	200	400	400	400	495	—	—
Alum . . .	100	100	100	100	100	100	—	—	—	100
Aluminium sulphate	—	—	—	—	—	—	120	120	68	—
Lead acetate . .	100	75	66·6	80	90	100	100	122·5	—	—
Sodium carbonate cryst. (10 aq.)	10	10	10	—	—	—	—	—	—	—
Chalk	—	—	—	—	—	—	8·5	7·9	8	6
Calcium acetate 24° Tw. (Sp. Gr. 1·12) . .	—	—	—	—	—	—	—	—	252	280

The red liquors of commerce are prepared by the double decomposition of normal aluminium sulphate and commercial acetate of lime. The so-called *common red liquor* contains a certain proportion of undecomposed aluminium sulphate, and is a crude sulphate-acetate, while in that known as *tin red liquor*, the decomposition has been made as complete as possible, so that it represents a crude normal aluminium acetate. These red liquors always possess a brownish appearance, from the presence of empyreumatic matter.

Application of the Aluminium Acetates and Sulphate-Acetates to the several Fibres.

102. *Application to Cotton.*—These are the aluminium mordants *par excellence* of the calico-printer. Their solutions are suitably thickened by means of flour, starch, or dextrin, and printed upon the calico and dried. Excessive heat in the drying must be carefully avoided (*e.g.*, by substituting hot plates, hot air, &c., for steam-heated cylinders), especially in the case of those mordants which are most readily dissociated (basic salts), otherwise poor and irregular colours are subsequently obtained. When this happens, it is said that the printed mordants have been "burned"; the mordant fixed upon the fibre has probably been dehydrated, or has undergone some physical change, which renders it less capable of attracting colouring matter in the subsequent dye-bath.

After "printing" and "drying" follows the so-called "ageing" process, which consists in exposing the printed goods in a more or less open or loose condition to an atmosphere of suitable temperature and hygroscopic state. The process has been made continuous by using the so-called "ageing machine," which is in reality a large chamber specially heated to 32°—38° C., and into which steam is admitted, so that a wet-bulb thermometer registers 4°—6° C. lower. The printed calico is drawn through this chamber, under and over a system of horizontal rollers situated at the top and bottom, at such a rate that the calico is exposed to the moist warm atmosphere for about twenty to thirty minutes. During this operation the starch, or other thickening, is more or less softened by the moisture, and the mordant permeates the fibres more thoroughly; large quantities of acetic acid are driven off, and a considerable amount of insoluble basic salt is fixed upon the cotton. Immediately on leaving this chamber the pieces are rolled up into loose bundles, and are allowed to remain for some time (twenty-four to forty-eight hours) in a warm room (32° C., dry bulb, 28° C., wet bulb) for the completion of the ageing process.

The next operation is that of "cleansing," or "dunging," in which the pieces are passed in the open width, for two minutes, through hot solutions containing one or more of the following ingredients: cow-dung, arsenate of soda, phosphate of soda, silicate of soda, chalk, &c.

The object of this cleansing operation is threefold: first, to fix more completely on the fibre that portion of the mordant which has escaped the action of the ageing process; secondly, to prevent the unprinted (unmordanted) portions of the cloth from becoming mordanted, and thus subsequently soiled, by reason of soluble mordant coming off the printed parts; and, lastly, to remove the thickening. The last object is more thoroughly attained by repeating the cleansing operation, but this time submitting the calico in the chain form to an intermittent and protracted process of squeezing between rollers. The most effectual method, however, of removing the thickening is to steep the cloth for an hour or two in an infusion of bran, the diastase ferment of which soon changes the insoluble starch into soluble glucose. After a thorough washing, the printed (mordanted) cloth is ready for dyeing.

Aluminium acetates are largely used in many of the so-called steam-colours of the calico-printers, *e.g.*, steam-alizarin-reds, &c. In the "colour," or thickened printing mixture, the aluminium acetate is merely mechanically mixed with the alizarin or other colouring matter; but when the printed material is subjected to the action of steam, decomposition of the mordant, its combination with the colouring matter, and the fixing on the fibre of the coloured compound produced, all take place simultaneously.

Experiment has shown that a pure aluminium acetate does not give such full rich colours as when a portion of the acetic acid is replaced by sulphuric, nitric, hydrochloric or hydrothiocyanic acid.

An aluminium sulphate-acetate represented by the formula $Al_2(SO_4)(C_2H_3O_2)_3(OH)$ seems to give the best results.

Aluminium acetates, &c., are also frequently used by the Turkey-red dyer to replace entirely, or in part only, the basic aluminium sulphates. No difference is made in the method of fixing from that usually adopted.

By the ordinary cotton-dyer these mordants are comparatively little employed, since, in the general method adopted of fixing by precipitation, they possess no advantage over the basic sulphates, and are more costly.

Sometimes they are used in conjunction with certain aniline colours. The cotton is worked in the colour solution, containing a certain proportion of aluminium acetate. During the gradual raising of the temperature of the bath, alumina is precipitated upon the fibre, and drags down along with it some colouring matter. The method does not yield fast dyes, and is in most cases irrational.

103. *Application to Wool.*—The aluminium acetates find no use in the mordanting of wool; they are too sensitive, and, consequently, deposit the mordant too much upon the surface of the fibre, making the wool harsh, and giving uneven colours.

104. *Application to Silk.*—The aluminium acetates are little used in mordanting silk, except in printing.

105. **Aluminium Thiocyanate (Sulphocyanide).**—This mordant is of comparatively recent introduction.

It is prepared by the double decomposition of aluminium sulphate, with barium or calcium thiocyanate.

$$\underset{\substack{\text{Aluminium}\\ \text{sulphate.}}}{Al_2(SO_4)_3\cdot 18H_2O} + 3[\underset{\substack{\text{Barium}\\ \text{thiocyanate.}}}{Ba(CNS)_2\cdot 2H_2O}] = \underset{\substack{\text{Aluminium}\\ \text{thiocyanate.}}}{Al_2(CNS)_6} + \underset{\substack{\text{Barium}\\ \text{sulphate.}}}{3BaSO_4}$$

$$+ \underset{\text{Water.}}{24H_2O}$$

Lauber and Hausmann give the following method of preparation: Dissolve five kilograms of aluminium sulphate in five litres of boiling water, add 250 grams of chalk, and then eleven and a half litres of crude calcium thiocyanate solution, 30° Tw. (Sp. Gr. 1·15), and stir well; let settle, filter, and use the clear solution. It can be concentrated by boiling down, *ad libitum*, if necessary, since it is not decomposed in this manner. Solutions of basic thiocyanates may be prepared by adding varying amounts of an alkaline carbonate to solutions of the normal salt. Solutions of the following have been prepared by Liechti and Suida: $Al_2(CNS)_5(OH)$, $Al_2(CNS)_4(OH)_2$, $Al_2(CNS)_3(OH)_3$, $Al_2(CNS)_2(OH)_4$.

With the exception of the first, solutions of all these basic salts precipitate on boiling, and increase of basicity renders the decomposition more complete. None are dissociated by merely diluting water.

Normal aluminium thiocyanate has hitherto only found use with the calico-printer for the production of steam alizarin reds. Its great advantage is, that not being an acid mordant (like the acetates which it replaces), it does not attack the steel "doctors"; the printing-colour remains, therefore, free from iron, and the ultimate colour is more certain of being clear and bright. Its high price has prevented it from being adopted in mordanting wool. It is, however, capable of giving good results. The wool simply requires to be introduced into a cold solution of the thiocyanate, which is then gradually heated to the boiling point in the course of 1—1½ hours.

There are no records of the employment of aluminium thiocyanate for silk.

106. Aluminium Chloride.—The normal salt, Al_2Cl_6, may be prepared by the double decomposition of barium- or calcium-chloride and aluminium sulphate, or by dissolving aluminium hydrate in hydrochloric acid. Solutions of basic salts may be prepared by adding the requisite amount of alkaline carbonate to a solution of the normal salt.

The following basic salts have been prepared in solution: $Al_2Cl_5(OH)$, $Al_2Cl_4(OH)_2$, $Al_2Cl_3(OH)_3$, $Al_2Cl_2(OH)_4$. None of these mordants are precipitated, either by heating or by diluting with water.

The first two of the above basic salts may also be made by dissolving aluminium hydrate in a hot solution of the normal salt, but if more $Al_2(OH)_6$ be added—*e.g.*, sufficient to form the basic salt $Al_2Cl_2(OH)_4$—not only does it not dissolve, but the precipitate increases, and the filtered solution contains equal molecules of the normal salt and of hydrochloric acid. It would appear as if the nascent $Al_2Cl_2(OH)_4$ had decomposed, according to the following equation :—

$$\underset{\substack{\text{Basic aluminium}\\\text{chloride.}}}{7Al_2Cl_2(OH)_4} + 2H_2O = \underset{\substack{\text{Aluminium}\\\text{hydrate.}}}{5\,Al_2(OH)_6} + \underset{\substack{\text{Aluminium}\\\text{chloride.}}}{2Al_2Cl_6} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2\,HCl.}$$

An *aluminium chloride-acetate*, $Al_2Cl_2(C_2H_3O_2)_4$, may be prepared according to the following equation :

$$\underset{\substack{\text{Aluminium}\\ \text{sulphate.}}}{Al_2(SO_4)_3\cdot 18\,H_2O} + \underset{\substack{\text{Lead}\\ \text{acetate.}}}{2[Pb(C_2H_3O_2)_2\cdot 3H_2O]} + \underset{\substack{\text{Barium}\\ \text{chloride.}}}{BaCl_2} = \underset{\substack{\text{Aluminium}\\ \text{chloride-acetate.}}}{Al_2Cl_2(C_2H_3O_2)_4}$$

$$+ \underset{\substack{\text{Barium}\\ \text{sulphate.}}}{BaSO_4} + \underset{\substack{\text{Lead}\\ \text{sulphate.}}}{2PbSO_4} + \underset{\text{Water.}}{24H_2O}$$

This mordant dissociates neither on heating nor on diluting with water, and yields to the cotton fibre, by steeping and drying, a remarkably low percentage of alumina, yet it is said to give excellent results in steam-alizarin-reds (calico-printing).

The aluminium chlorides are seldom used as mordants.

107. Aluminium Nitrate.—The normal salt $Al_2(NO_3)_6$ is prepared by the double decomposition of aluminium sulphate and lead nitrate, or by dissolving the requisite amount of aluminium hydrate in nitric acid. Basic mordants are prepared by adding an alkaline carbonate to a solution of the normal salt. None of these are dissociated, either by heating or by diluting with water.

Aluminium nitrate is not much employed as a mordant. It finds a limited use in the production of yellow shades of steam-alizarin-reds, and some other steam colours.

In mordanting wool or silk it is not used.

108. Aluminium Oxalate and Tartrate.—These mordants may be prepared by dissolving aluminium hydrate in the respective acids. As such, they find only a limited use in certain steam colours of the calico-printer.

Although not used directly in mordanting wool, it is very probable that whenever potassium hydrogen tartrate (cream of tartar) is used along with aluminium sulphate, there is produced aluminium tartrate, which may be considered as the real mordanting salt.

In mordanting silk these salts are not used.

109. Aluminium Thiosulphate (Hyposulphite).—This mordant may be prepared by the double decomposition of aluminium sulphate and calcium thiosulphate (CaS_2O_3). Its use was proposed long ago by Kopp, who claimed for it the following advantages, that it was cheaper than aluminium acetate, gave fuller colours, fixed alumina on the fibre better, and prevented the fixing of iron, *i.e.*, prevented its oxidation. Although capable of being used instead of aluminium acetate for dyed-alizarin-reds by the calico-printer, its employment has scarcely passed the experimental stage. Quite recently, however, a solution containing alum and sodium thiosulphate has been proposed for mordanting silk previous to dyeing with Alizarin, Alizarin Blue, Cœruleïn, &c., and it is said to have yielded good results on the large scale.

110. Aluminate of Soda ($Al_2Na_2O_4$).—This mordant, also called "alkaline-pink mordant," is best prepared by dissolving aluminium hydrate in caustic soda to the point of saturation. Another method is to add caustic potash to a hot solution of aluminium sulphate, until the precipitate at first formed is exactly re-dissolved ; on cooling, most of the potassium sulphate crystallises out; or heat together, for example, 350 grams of aluminium sulphate and 1 litre of caustic potash, 54° Tw. (Sp. Gr. 1·27), and cool, in order to allow the potassium sulphate to crystallise out. The solution thus obtained stands at 30° to 36° Tw. (Sp. Gr. 1·15—1·18). Slight excess of alkali renders the solution more stable, and is not injurious.

This mordant finds only a very limited use in calico-printing. It is thickened with dextrin.

Its advantages are that it is not liable either to yield bad colours through being dried on the fibre at too high a temperature, or to contract iron stains. Its chief defect is that it cannot be associated with acid mordants.

After printing and drying, the alumina is fixed on the fibre by mere exposure to the atmospheric carbonic acid, or by passing the printed cloth, for two minutes, through a solution of ammonium chloride 10° Tw.

(Sp. Gr. 1·05), heated to 50°—60° C. Excessive accumulation of ammonia in the bath should be avoided, since it is apt to dissolve some of the alumina from the cloth.

Zinc sulphate or chloride may replace ammonium chloride for fixing purposes, but it possesses no advantages.

Aluminate of soda, owing to its alkalinity, is not used as a mordant for wool and silk.

IRON MORDANTS.

These are scarcely less important than the aluminium mordants, being used for all fibres; they may also claim equal antiquity. Unlike the aluminium mordants, those of iron may occur in two states of oxidation, namely, as *ferrous* and as *ferric* salts.

111. Ferrous Sulphate ($FeSO_4 \cdot 7H_2O$).—This mordant is also known as *green vitriol* or *copperas.* It is largely prepared by dissolving scrap-iron in dilute sulphuric acid, and allowing the solution to crystallise; also by the natural oxidation of iron pyrites, and as a by-product in the manufacture of alum and copper sulphate. When exposed to the air, the pale-green crystals gradually become coated with brown, insoluble, basic ferric sulphate. Large crystals are apt to enclose mechanically some of the acid mother-liquor. The presence of copper and alumina is to be avoided.

A solution of ferrous sulphate is not precipitated either by heating or by diluting with water, if access of air be prevented.

Application of Ferrous Sulphate to the various Textile Fibres.

112. *Application to Cotton.* — The employment of ferrous sulphate, as such, in mordanting cotton is somewhat limited. When used, it is generally applied as a "saddening" agent, *i.e.*, *after* the application of the colouring matter, in which case it forms a lake with whatever colouring matter the cotton has absorbed. After boiling the cotton with a decoction of the colouring matter, excess of the liquor is wrung out, and the cotton is then worked in a cold solution of ferrous sulphate. The process may be repeated. This mode of procedure is somewhat irrational, because the amount of colouring matter which unmordanted cotton absorbs is, as a rule, very small; hence the method is suitable only for very pale shades.

A better method of employing this mordant is to impregnate the cotton with tannin matter, and afterwards steep it in a solution of ferrous sulphate, but for this mode of dyeing the ferric salt is preferable.

Ferrous sulphate is used for the production of iron buffs on cotton in the same manner as ferric nitrate (*see* p. 191). It is also used for saddening or darkening the colours yielded by certain coal-tar colouring matters which have been fixed by means of tannic acid.

113. *Application to Wool.*—Ferrous sulphate is still used as a mordant in wool dyeing, but it has been very largely displaced by potassium dichromate. Although it is quite possible to mordant wool by boiling it with a mixture of ferrous sulphate and cream of tartar in suitable relative proportions, good bright colours are obtained only when a somewhat large amount of "tartar" is used, so that this method becomes costly. There is also the danger that the wool will be unevenly mordanted, unless great care is taken to raise the temperature of the mordanting bath very gradually to the boiling point. *Without* the addition of "tartar," the wool acquires a deep reddish-brown colour, through precipitation of ferric oxide, or a basic sulphate; *with* the addition, the wool acquires a pale yellowish colour.

The most generally adopted method of applying ferrous sulphate is, first to boil the wool with a decoction of the colouring matter until a sufficient amount has been absorbed, and then to add ferrous sulphate to the same bath, in the proportion of 5—8 per cent. of the weight of wool, and to continue the boiling for half an hour or so longer (saddening).

With some colouring matters—*e.g.*, Camwood and Catechu—the boiling with ferrous sulphate is best performed in a separate bath.

114. *Application to Silk.*—Ferrous sulphate, as such, is not much used in mordanting silk. In the dyeing of English black (*noir Anglais*), the silk is mordanted by working it at 60° C. in a bath containing a solution of 50 per cent. Logwood, 50 per cent. Old Fustic, 5—6 per cent. ferrous sulphate, and 2—3 per cent. acetate of copper. It is afterwards dyed in a bath of Logwood and soap. (*See* also p. 333.)

115. **Ferrous Acetate.**—This mordant may be prepared by the double decomposition of ferrous sulphate and lead or calcium acetate. The solution thus obtained does not keep well; it rapidly becomes oxidised, basic ferric acetate being deposited.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Calcium}\\\text{acetate.}}}{Ca(C_2H_3O_2)_2} = \underset{\substack{\text{Ferrous}\\\text{acetate.}}}{Fe(C_2H_3O_2)_2} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4}.$$

A much more generally useful mordant, and one which is manufactured on an extensive scale, is the so-called *pyrolignite of iron*, *iron liquor*, or *black liquor.*

It is prepared by saturating crude acetic acid, 4°—8° Tw. (Sp. Gr. 1·02—1·04), (pyroligneous acid), with iron turnings, until the dark olive liquid stands at about 20° Tw. (Sp. Gr. 1·1.); sometimes it is concentrated to 30° Tw.

This mordant is generally understood to be a crude ferrous acetate, containing a certain amount of tarry matter, which prevents it from oxidising rapidly. According to Moyret, however, it is a mixture of the ferrous salt with a salt of Fe_3O_4 (magnetic oxide), and he considers that to the presence of this latter its good qualities are due.

Moyret further maintains that it does not necessarily contain tarry matter, but pyrocatechin, $C_6H_4(OH)_2$, the iron salt of which is dark green, and he attributes the slowness of oxidation of the mordant to the presence of this reducing agent.

116. *Application to Cotton.*—Pyrolignite of iron is the iron mordant most largely used by the calico-printer for dyeing blacks, purples, chocolates, &c.

The mode of fixing by "ageing" and "cleansing" is identical with that employed with the aluminium acetates (*see* p. 169). To obtain the best results, the mordant must be applied to the calico as much as possible in the ferrous state.

During the ageing process, a variable proportion of acetic acid escapes, but it is accompanied by oxidation of the remaining compound, and care must be taken that this latter does not proceed too rapidly or continue too long. If the oxidation were effected rapidly—*e.g.*, by steaming, or by passing through solutions of potassium dichromate or bleaching-powder—the results would be unsatisfactory. According to Schlumberger, the normal state of oxidation for good results is that intermediate between ferrous and ferric oxide. Various additions have been made to this iron mordant, with a view to retard and render incomplete, or to make more regular, its oxidation during "ageing"; that which has found most favour is arsenious acid, either dissolved in a mixture of acetic acid and common salt or ammonium chloride, or in the form of sodium arsenite. Since glycerine acts in the same way, a solution of arsenious acid in glycerine would probably be an excellent addition. Such solutions have received the name of "purple fixing liquors," or simply "fixing liquors," since they are almost invariably mixed with the mordant by the calico-printer for the production of dyed alizarin-purples.

Iron liquor at about 6° Tw. (Sp. Gr. 1·03), properly applied to calico gives a black on dyeing with Alizarin; from 4° Tw. (Sp. Gr. 1·02) downwards to a very diluted state, it yields various shades of purple or lilac; mixed with red liquor, and dyed subsequently with Garancine or Alizarin, with the addition of Sumach and Quercitron Bark, it gives chocolate colours.

Pyrolignite of iron is not extensively used by the general cotton-dyer, principally because it is more expensive than the "nitrate of iron" usually employed, and because in many cases it yields only slightly better results.

It is best applied by impregnating the cotton with a solution of tannin matter of suitable concentration; after removing excess of liquid by squeezing, the cotton is worked and steeped in a cold solution of the iron mordant at 2°—6° Tw. (Sp. Gr. 1·01—1·03) for one hour or more, and finally washed. The concentration of the tannin bath determines the amount of iron fixed on the cotton. Since iron mordants are invariably used for the production of dark, dull, or sad colours, this method of fixing them by means of tannin tends to save colouring matter, because the dark colour of the tannate of iron is added to that of the colour subsequently imparted.

117. *Application to Wool.*—Pyrolignite of iron is not employed in wool dyeing, though it might possibly be used with advantage in some cases—*e.g.*, in the black dyeing of skin mats, &c.—where only low temperatures in the baths are admissible. A mixture of ferrous sulphate and sodium acetate might be used instead of the pyrolignite.

118. *Application to Silk.*—Pyrolignite of iron is largely employed in the black dyeing and weighting of raw-silk fringes, &c.; its application is always preceded by a tannin bath. The silk is first impregnated at 40°—45° C., with an infusion of tannin matter, 100 per cent. (preferably chestnut extract), then worked at 50°—60° C. in a bath of pyrolignite of iron (Fr: *pied de fer*) 12°—14° Tw. (Sp. Gr. 1·06—1·07), and finally exposed to the air. These operations may be repeated from two to fifteen times, both to give body of colour and to add weight, which latter may vary from 30 to 400 per cent. of the weight of the silk. The mordanting bath is maintained at the requisite degree

of concentration by fresh additions of pyrolignite of iron; its acidity, which increases with use, is neutralised by occasionally adding iron turnings, and heating the bath to near the boiling point. Too frequent use of the bath must be avoided, in order to give the added iron time to dissolve. The scum produced in heating must be removed.

Pyrolignite of iron gives a bluish-black difficult to obtain by using other iron salts. The blue tone seems to be acquired through oxidation, and since the rate at which this proceeds depends upon many factors, the colour is very liable to be irregular.

Although pyrolignite of iron has been employed in the above manner for boiled-off silk, it is now entirely replaced for this, by basic ferric sulphate (nitrate of iron).

Sometimes a weak pyrolignite of iron bath is employed in black silk dyeing, between two catechu baths, in order to alter the tone of colour.

119. Ferrous Nitrate and Ferrous Chloride do not seem to have been generally adopted as mordants. The latter is used under the name of "muriate of iron," in the preparation of a logwood black printing colour for woollens.

120. Ferrous Thiosulphate (Hyposulphite) has been recommended as a good iron mordant for cotton, but it has not been adopted in practice. It is produced by the double decomposition of ferrous sulphate and calcium thiosulphate. When dried on the fibre, it decomposes with final production of basic ferric sulphate.

121. Ferric Sulphate. "Nitrate of iron."—A solution of normal ferric sulphate $Fe_2(SO_4)_3$ may be prepared according to the following equation:—

$$\underset{\substack{\text{Ferrous}\\ \text{sulphate.}}}{6FeSO_4 \cdot 7H_2O} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{2HNO_3} = \underset{\substack{\text{Ferric}\\ \text{sulphate.}}}{3Fe_2(SO_4)_3} + \underset{\substack{\text{Nitrogen}\\ \text{dioxide.}}}{2NO} + \underset{\text{Water.}}{46H_2O}$$

The ferrous sulphate is dissolved in water containing the calculated amount of sulphuric acid, the solution is gently heated and the necessary quantity of nitric acid is added gradually. If the solution is sufficiently concentrated it may be boiled in order to complete the reaction.

The nitric acid merely acts as an oxidising agent, thus :—

$$2HNO_3 = H_2O + 2NO + O_3$$

hence the usual name given to this preparation, "nitrate of iron," is a misnomer.

By adding an alkaline carbonate to solutions of the normal salt of suitable concentration, it is possible to obtain solutions of basic ferric sulphates, *e.g.*, $Fe_2(SO_4)_2(OH)_2$ and $Fe_4(SO_4)_3(OH)_6$, both of which, however, readily decompose on standing for a few hours.

A soluble basic sulphate of greater stability is prepared by adding a suitable amount of hydrated ferric oxide to a solution of the normal salt. It is, however, more economical to adopt the method described for the normal salt, but using only half the amount of sulphuric acid, thus :—

$$\underset{\text{Ferrous sulphate.}}{12FeSO_4{\cdot}7H_2O} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Basic ferric sulphate.}}{3Fe_4(SO_4)_5(OH)_2} + \underset{\text{Water.}}{86H_2O} + \underset{\text{Nitrogen dioxide.}}{4NO}$$

In making this preparation on a small scale, it will be noticed that at first, even after the whole of the requisite nitric acid has been added, the solution has a dirty olive-brown colour, which is indicative of the presence of ferrous salt. When, however, the boiling liquid has attained a certain degree of concentration, complete oxidation suddenly takes place, there is a copious evolution of red fumes, and the liquid at once assumes the normal orange yellow colour of the ferric salt solution.

This basic ferric sulphate (Fr. *rouille*) is sold very largely to black silk-dyers, as a deep red liquid of about 70°—85° Tw. (Sp. Gr. 1·35—1·4). It is made in large covered stone vats provided with a wide tube for the disengagement of the nitrous fumes, a small tube for the introduction of the acids, and a large opening for introducing the ferrous sulphate, and stirring the mixture. For every 100 kilos. of basic sulphate at 84° Tw. (Sp. Gr. 1·42) required, 80 kilos. of ferrous sulphate are employed; these are put into the vat, and a mixture, slightly diluted with water, containing 10—15 per cent. of nitric acid 72° Tw., and 6—7 per cent. of sulphuric acid 168° Tw., is run in gradually. The whole is well stirred, and the reaction is allowed to proceed in the cold; when this primary reaction has subsided it is completed by blowing in steam. The nitrous fumes, which are given off in large quantities, are condensed and collected. When no more are evolved, the reaction is complete, and the liquid is transferred to large tanks to cool and settle.

It was formerly thought that the presence of small proportions of ferrous sulphate and nitric acid were beneficial in the production of the best black on silk, but this was a mistake. A good sample of this mordant should not be precipitated by silver nitrate. Potassium ferricyanide should, with a dilute solution, give at most a blue coloration, but no precipitate. Submitted to desiccation and calcining, it should leave about 17 per cent. ferric oxide. It is dissociated by diluting with water, an insoluble and still more basic ferric sulphate being precipitated, while a more acid salt remains in solution.

Since it sometimes happens that two preparations having the same chemical composition give different results in dyeing, it is supposed that there are isomeric compounds due to the different temperatures at which the oxidation may take place.

Great care is required in its manufacture, since if it is too basic it tarnishes the lustre of the silk, and if too acid it does not give up its oxide to the fibre in sufficient quantity.

122. *Application to Cotton.*—The normal ferric sulphate is seldom used.

The above-mentioned soluble basic ferric sulphate, or even a slightly more acid compound, is used in dyeing cotton black. The cotton is first impregnated with an infusion of tannin matter, and either at once, or after passing through lime-water, it is worked and steeped for about one hour in a solution of the mordant, at a strength of 2°—4° Tw. (Sp. Gr. 1·01—1·02). It is finally washed, either in water only, or in such as contains a small addition of ground chalk, for the purpose of completing the precipitation of basic salt on the fibre, and to remove all acidity. The cotton is subsequently dyed in a logwood bath.

In this process the tannic acid, which is absorbed and attracted by the cotton, serves principally to fix the iron mordant, although it incidentally produces a bluish-black colour by combining with the ferric oxide or basic ferric salt. The passing through lime-water after the tannin bath evidently forms a calcium tannate, and the decomposition of the ferric salt is thereby facilitated, since the lime combines with its sulphuric acid. This mordant may also be used for dyeing iron buffs in the same way as ferric nitrate (*see* p. 191).

123. *Application to Wool.*—The ferric sulphates do not appear to have been utilised hitherto in the mordanting of wool, although it seems possible that they might be useful if properly applied.

124. *Application to Silk.*—The soluble basic ferric sulphate $Fe_4(SO_4)_5(OH)_2$ is the iron mordant *par excellence* of the black-silk dyer.

In mordanting raw silk, the latter is first worked in a tepid bath (40°—50° C.) of sodium carbonate, washed and well wrung out, and then worked in a cold solution of the mordant at 15° Tw. (Sp. Gr. 1·075) for ½—1 hour. The silk is then drained, wrung out, well washed, wrung out again, and worked for about half an hour in a tepid (40°—56°C.) solution of sodium carbonate. It is finally wrung out and well washed. These several operations may be repeated three or four times, according to the colour and weight required.

In mordanting boiled-off silk, the material is worked for ½—1 hour in a cold solution of the basic ferric sulphate at about 50° Tw. (Sp. Gr. 1·25), excess of liquid is then removed by squeezing and wringing, and the silk is well washed—first with cold water, and finally with tepid water. These operations may be repeated as many as seven or eight times, after which the silk is worked at 100° C., in an old soap-bath, or one containing "boiled-off" liquor, to which about 12 per cent. (of the weight of silk) of oleïn soap and 2 per cent. of sodium carbonate crystals are added. A final washing completes the mordanting process. The iron and soap baths are permanent, care being taken, by making fresh additions of mordant, to maintain regularly the concentration of the former, and to boil up the latter before mordanting each lot of silk, in order to bring to the surface and then skim off the iron soap which has been formed during a previous operation.

It is essential that silk mordanted in basic ferric sulphate should not be allowed to dry in the mordanted state. It should either be left steeping in the strong mordant, or left, after washing, well covered up with wet sheets.

Silk strongly impregnated with ferric oxide is gradually destroyed on keeping, slow combustion or oxidation of the fibre being induced.

The theory relative to the above methods of mordanting is as follows:—

In the case of raw silk, where a comparatively weak solution of the ferric sulphate is employed, apart from general absorption of the liquid, the silk-gum itself causes decomposition and precipitation of an insoluble basic salt throughout its mass during the steeping operation. The washing in water, and rinsing in sodium carbonate, complete the decomposition, and remove the necessarily liberated acid salt.

In the case of boiled-off silk, the fibre simply absorbs the liquid during the steeping in the concentrated solution of mordant, decomposition and precipitation of basic salt only taking place during the washing process,

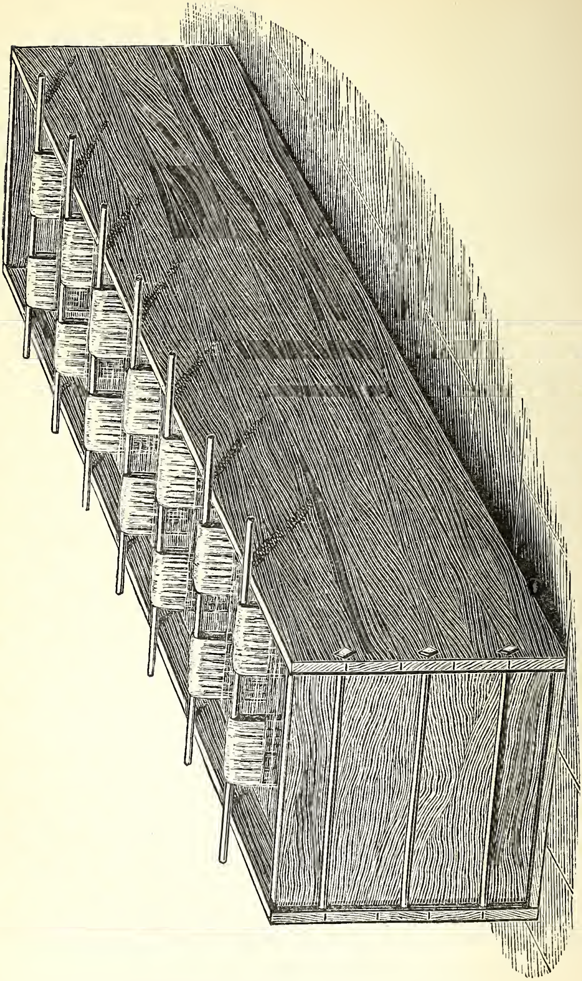


Fig. 45.—Mordanting Bath for Silk.

which, of course, also removes the acid salt formed. The employment of water containing bicarbonate of lime is exceedingly advantageous for the washing, since it greatly facilitates the decomposition of the absorbed mordant.

The boiling in soap solution is necessary to complete the decomposition of the absorbed mordant, and the temperature employed, 100° C., is said to modify the precipitated ferric oxide and render it less liable to dissolve in the successive iron baths.

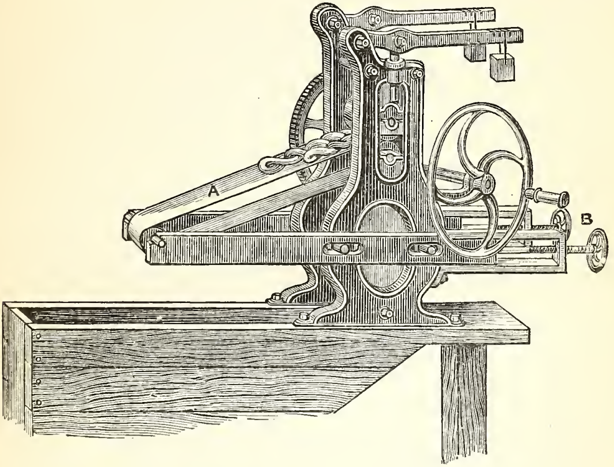


Fig. 46.—Squeezing Machine used in the Mordanting of Silk.

According to Moyret, no iron soap is precipitated on the silk in this operation.

Previous impregnation of the silk with tannin matter does not tend to cause a larger precipitation of mordant on the fibre, but rather the reverse; indeed, the silk loses weight through the oxidation and destruction of the absorbed tannic acid.

By one complete mordanting operation the silk gains about 4 per cent. in weight. If the operations are repeated six times, it gains about 25 per cent., or has about made up the loss sustained in boiling-off. If repeated seven to eight times, there is a gain of about 8 per cent. of the original weight of the raw silk. Thus mordanted, the silk possesses a deep orange brown colour, and still retains its lustre.

Fig. 45 represents the mordanting bath in general use with black silk dyers.

It consists of a rectangular wooden vat, for holding the iron mordant. The silk, properly suspended on smooth wooden rods (*e.g.*, hickory sticks with the bark peeled off), is turned in the solution by hand. After draining, the excess of liquid is removed by passing the hanks singly through a squeezing machine (Fig. 46), provided with an inclined, broad, endless band of india-rubber, A, which carries the hanks laid thereon through the india-rubber rollers. By means of the screws at B the endless band, A, can always be kept in a state of proper tension. A more complete expression of the liquid is effected afterwards by twisting the hanks vigorously by hand.

The washing machine employed is illustrated in Fig. 47, which represents one constructed by Gebrüder Wansleben, of Crefeld. It consists of a double row of glazed, fluted, porcelain reels, on which the hanks of silk are suspended and made to revolve. The reels are geared together by a series of cog-wheels, one of which, on each side, is driven by a cog-wheel attached to a central friction disc.

The washing is effected by water-pipes, situated below the reels, and perforated on both sides horizontally. A similar water-pipe is situated between each pair of hanks, so that each one during its revolution has a continuous and uninterrupted stream of water-jets playing upon it, both internally and externally.

In order to prevent the fibres from becoming en-

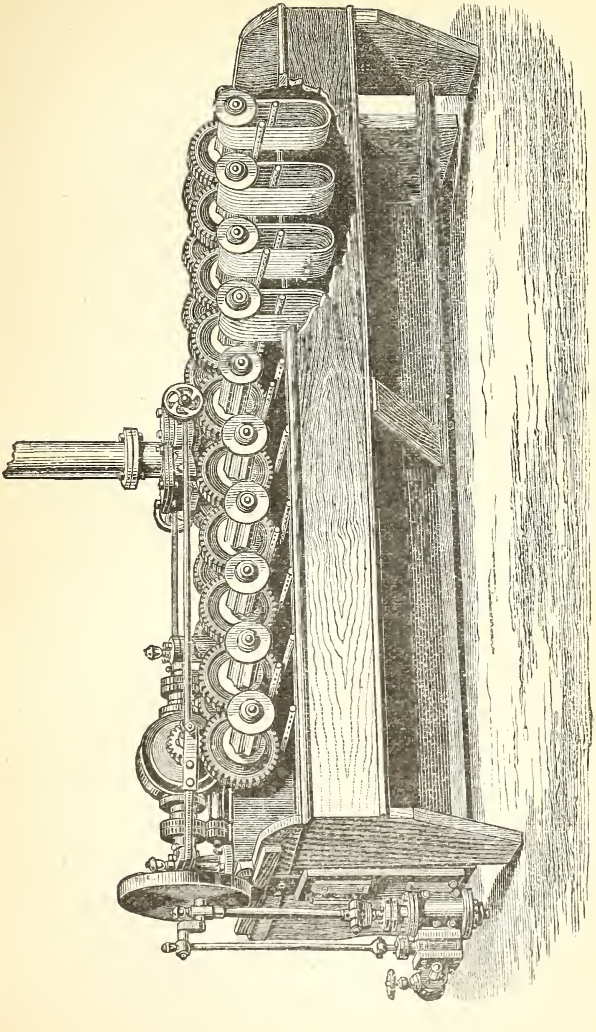


Fig. 47.—Washing Machine used for Silk.

tangled, the reels are automatically caused to revolve alternately to the right and left. The movement of a single lever sets the reels in motion, and turns on the water. The reels on each side can be worked independently of each other, so that while one set are in action and washing, the other can be emptied of hanks and refilled.

After washing with cold water in the above manner, an additional washing or rinsing with warm water is effected in a wooden trough, situated between and below the two sets of reels. By means of a counterpoise, it can be readily brought below either set of hanks, so that they may then revolve in the warm water. The trough is fed from a tank placed at a higher level, where the water is specially heated by steam to the requisite temperature.

125. Ferric Nitrate-sulphates.—Several of these are made and employed in practice under the name of *nitrate of iron.*

They are produced whenever ferrous sulphate is oxidised by means of nitric acid, after the manner already described for the production of ferric sulphates (*see* pp. 181, 182), but the sulphuric acid which was there added is here entirely or partially replaced by nitric acid, thus :—

$$\underset{\text{Ferrous sulphate.}}{6FeSO_4\cdot 7H_2O} + \underset{\text{Nitric acid.}}{6HNO_3} + 2HNO_3 = \underset{\text{Ferric-nitrate-sulphate.}}{3Fe_2(SO_4)_2(NO_3)_2} + \underset{\text{Nitrogen dioxide}}{2NO} + 46H_2O$$

$$12FeSO_4\cdot 7H_2O + 6HNO_3 + 4HNO_3 = \underset{\text{Basic-ferric-nitrate-sulphate.}}{3Fe_4(SO_4)_4(NO_3)_2(OH)_2} + 4NO + 86H_2O$$

The composition of those used in practice is very variable. Compounds of definite composition are not generally intended to be made, and their value as mordants is entirely determined by the results they yield in dyeing.

They are deep brownish-red solutions, and contain frequently some ferrous salt which has escaped oxidation, and which, in many cases, is not considered injurious.

In conjunction with Logwood, for example, pure ferric salts tend to give brownish-blacks, while the ferrous salts give bluish-blacks. A mixture of the two is therefore considered to give a more pleasing jet-black.

Excess of acid should be avoided when these mordants are applied to cotton, especially in printing colours which require steaming.

If used for purposes of "saddening," a slight acidity may, on the other hand, be beneficial, since the mordant is then more slowly decomposed, and more likely to penetrate the fibre and to give a regular mordanting. If too basic, on the contrary, the mordant is too sensitive, decomposes spontaneously, and gives irregular work.

126. *Application.*—The principal application of the nitrate-sulphates of iron is in the black dyeing of cotton.

The mode of application is identical with that given for the ferric sulphates. (*See* p. 183.)

In wool dyeing, the above mordants are not used, and in silk dyeing they have been supplanted by the soluble basic ferric sulphate.

127. Ferric Nitrate.—This mordant constitutes the true *nitrate of iron* of the dyer, and is prepared by dissolving scrap-iron slowly in nitric acid. As soon as there is a sensible deposit of insoluble basic ferric nitrate the addition of iron is discontinued, and the liquid is allowed to settle. According to the proportion of nitric acid used, and the care taken in the preparation, the composition will be very variable.

It finds a comparatively limited use now, being employed only in cotton dyeing, *e.g.*, in the production of buff shades. The cotton is impregnated with a solution of nitrate of iron, and, after removing excess, is passed through a cold solution of sodium carbonate, whereby ferric oxide is precipitated. It is also used occasionally for blacks.

128. Ferric Acetate.—The normal acetate, $Fe_2(C_2H_3O_2)_6$, is prepared by the double decomposition of ferric sulphate and lead acetate, in suitable proportions.

On neutralising a solution of the normal acetate with increasing amounts of an alkaline carbonate, solutions of various basic acetates are obtained, *e.g.*, $Fe_2(C_2H_3O_2)_5(OH)$, $Fe_2(C_2H_3O_2)_4(OH)_2$, $Fe_2(C_2H_3O_2)_3(OH)_3$; $Fe_2(C_2H_2O_2)_2(OH)_4$. A solution of the normal salt is not dissociated either by heating or diluting with water; solutions of the basic salts are, however, dissociated on heating, but not by dilution. Increase of basicity lowers the dissociation temperature. It is remarkable, however, that when the solutions are diluted, the point of dissociation by heating is raised in the least basic mordant, $Fe_2(C_2H_3O_2)_5(OH)$, remains unchanged in the case of $Fe_2(C_2H_3O_2)_4(OH)_2$, and is lowered only in the more basic mordants. (Liechti and Suida.)

129. *Application.*—The ferric acetates seem to find, at present, little or no use as mordants, although some were formerly employed rather largely in black silk dyeing.

130. **Ferric sulphate-acetates** have occasionally been used, having been incidentally prepared through the desire of reducing the excessive acidity of ferric sulphates by the addition of lead acetate.

131. **Ferric Acetate-Nitrate**, or *ferric nitrate-acetate.*—This mordant has also been incidentally prepared by adding a certain proportion of lead acetate to solutions of certain ferric nitrate-sulphates with a view to reduce their acidity. A product of this nature has, however, been much used in silk dyeing, and is still employed in the dyeing of black silk intended for plush (*e.g.*, for hats), since the colour which it yields is not affected by hot-pressing or ironing. Its mode of preparation, for a long time kept secret, is as follows: iron turnings are dissolved in nitric acid, as in the manufacture of ferric nitrate, but the addition of iron is continued until the whole becomes a pasty mass of insoluble basic ferric nitrate. This basic precipitate is collected and dissolved in hot acetic acid, taking care to leave a slight excess of the

precipitate. The deep red solution thus obtained is allowed to cool and settle.

132. Ferric Chloride.—The normal compound, Fe_2Cl_6, is not used as a mordant. Basic salts may be produced by dissolving hydrated ferric oxide in solutions of the normal salt, but these, too, have as yet found no use in practice.

133. Alkaline Iron Mordants.—Although hydrated ferric oxide is not soluble in caustic alkalis, the addition of certain organic substances (tartaric acid, glucose, glycerine, &c.) to the solution of a ferric salt, prevents the precipitation of the ferric oxide by alkali, and hence an alkaline solution of iron can be thus obtained. Take, for example, 2½ litres of ferric sulphate solution, equivalent to 1,250 grams of ferrous sulphate, add 1 litre of glycerine and 10 litres of caustic soda, 70° Tw. (Sp. Gr. 1·35); the solution has a deep reddish-brown colour. An alkaline ferric solution is also obtained by adding an excess of a concentrated potassium carbonate solution to a concentrated solution of ferric sulphate or nitrate. The precipitate which at first forms is re-dissolved under the above conditions.

Pyrophosphate of iron, $(Fe_2)_2(P_2O_7)_3$, is soluble in ammonia. Cotton mordanted by means of this alkaline solution is said to give good purples when dyed with Madder or Alizarin.

It has been noticed by Burgemeister that an addition of glycerine to a solution of ferrous sulphate prevents the precipitation of oxide by alkali, and that this alkaline solution is capable of mordanting cotton. Mix, for example, 1 kilo of ferrous sulphate, 2 litres of glycerine, and 60 litres of caustic soda, 70° Tw.

Notwithstanding the above facts, alkaline iron mordants have as yet received no practical application by the dyer, no doubt because of their excessive alkalinity and cost.

134. Iron Alum.—This salt, $\left.\begin{matrix}K_2\\ Fe_2\end{matrix}\right\}(SO_4)_4\cdot 24H_2O$, is exactly analogous to ordinary alum, and may be applied in the same way. Its use hitherto has been limited, having been confined to mordanting wool for dyeing with alizarin colours. There is no reason, however, why it should not find a more extended use.

TIN MORDANTS.

135. Tin.—Tin may occur in two states of oxidation—as stannous oxide, SnO, and as stannic oxide, SnO_2. These oxides, in their hydrated state, $Sn(OH)_2$ and $Sn(OH)_4$, are soluble either in acids or in caustic alkalis, and thus give rise to corresponding stannous and stannic salts, either of an acid or of an alkaline nature. Apart from their character as mordants, the stannous salts act as powerful reducing agents; they have a great avidity for oxygen, and tend to change into stannic compounds. This fact should always be borne in mind by the textile colourist, since it sometimes excludes them from being used in conjunction with other mordants of an oxidising character, or with such colouring matters as are decolorised by a reducing action. In particular cases, however, this characteristic may be made to serve a useful purpose, for example, in the reduction of indigo-blue to indigo-white, the discharging of iron buffs, manganese browns, &c., in calico-printing.

As a general rule, the stannous salts are employed for wool, and the stannic salts for cotton; the colours they yield with polygenetic colouring matters are usually remarkable for their brilliancy.

Solutions of the stannous and stannic salts are colourless. Many of the tin solutions, however, which the dyer prepares by means of nitric acid, with or without the addition of hydrochloric acid or alkali chlorides, possess a very decided yellow colour, and they seem to be of a more unstable character than the ordinary compounds. Hence some consider that these represent solutions of tin in an intermediate state of oxidation, namely, as sesquioxide, Sn_2O_3. It is, however, more probable that this coloration and sensibility are due to the presence of a peculiar modification of stannic oxide called metastannic acid.

136. Stannous Chloride.—This mordant is sold in the crystalline form ($SnCl_2 \cdot 2\,H_2O$) under the name of "tin crystals" or "tin salt." A good sample should contain 52 per cent. of tin. It is prepared by dissolving granulated tin in hydrochloric acid with the aid of heat, and allowing the concentrated liquid to crystallise.

$$Sn + 2HCl + 2H_2O = SnCl_2 \cdot 2H_2O + H_2$$

Access of air is said to facilitate solution, so that it may also be effected without heat if the acid is poured successively on exposed heaps of feathered tin.

$$Sn + 2HCl + 2H_2O + O = SnCl_2 \cdot 2H_2O + H_2O$$

Very frequently the solution is not crystallised; it is then sold under the names of "single muriate of tin" and "double muriate of tin," according as the Specific Gravity is 1·3 or 1·6 (60° Tw. or 120° Tw.).

These "muriates of tin" differ frequently, however, in concentration, from the standards here given; the amounts of tin, and the free acid which they always contain, vary considerably, and can only be determined by analysis. They are occasionally subjected to adulteration.

"Tin crystals" dissolve in a small quantity of water without undergoing decomposition, and a clear solution is obtained; on further dilution, however, this becomes turbid through the formation of an insoluble basic chloride or oxychloride [$2Sn(OH)Cl \cdot H_2O$] which is precipitated.

$$3SnCl_2 + 2H_2O + O = \underbrace{2Sn(OH)Cl \cdot H_2O}_{\text{Basic stannous chloride.}} + SnCl_4$$

The precipitate re-dissolves on the addition of hydrochloric acid. A similar oxidation takes place when "tin crystals" are kept for a lengthened period, especially if exposed to air and light. Owing to the presence of excess of acid, the "muriates of tin" are less readily decomposed by dilution with water.

137. *Application to Cotton.*—"Tin crystals" are largely used by the calico-printer for mixing with thickened aluminium mordants. When used in small amount, this addition prevents, probably by reason of its reducing action, the fixing of iron accidentally present in the printing colour, or acquired during the processes of printing, &c. It thus preserves the purity and brilliancy of dyed alizarin-reds, &c. When the addition is made in larger amount, it causes the printed mordant to resist iron mordants (covers) which are printed over it.

"Tin crystals" enter also into the composition of some "steam colours" along with dyewood extracts and such assistants as cream of tartar, oxalic acid, &c., *e.g.*, in steam cochineal red, steam yellow, &c.

Lakes produced by means of stannous chloride and certain dyewood extracts, sold under the name of "carmines," *e.g.*, Persian Berry carmine, Cochineal carmine, &c., are occasionally used in calico-printing.

As a mordant, and used alone, stannous chloride finds little employment in cotton dyeing. It is rather made use of to modify and brighten colours in which other mordants play the principal part. In Turkey-red dyeing, "tin crystals" are added in small proportion to the soap solution with which the dyed cotton is boiled in the process of "clearing," for the purpose of giving more brilliancy to the colour. Care must be taken not to add it in excessive quantity, otherwise an insoluble and sticky tin-soap is produced, and this adheres to and spoils the goods.

138. *Application to Wool.*—Stannous chloride in any of its forms may be and is used as a suitable mordant for wool, principally in conjunction with Cochineal for scarlet, and with Flavin, &c., for yellow or orange colours. With some colouring matters it is not necessary to be applied to the textile materials separately, but is introduced at once into the dye-bath along with the colouring matter and such assistants as cream of tartar,

oxalic acid, &c. This is rendered possible because the tin-lakes produced are for the most part dissolved in the excess of acid mordant present, from which they are absorbed by the wool.

When the wool is mordanted before dyeing, it is boiled with a solution of stannous chloride and cream of tartar. Applied in this way, it is not advisable to use more than 4—6 per cent. of tin crystals, since the wool tends to become harsh and tender, and its property of felting or milling is impaired. When applied in a more acid bath—*e.g.*, simultaneously with the colouring matter as described above—less mordant is probably fixed upon the wool, and the tendency to harshness in feel of the latter is not so apparent.

Stannous chloride is sometimes added to the dye-bath towards the end of the dyeing operation for the purpose of modifying the colour. Since the colour is thereby rendered lighter and brighter, this application is technically termed "blooming."

The tin-lakes of dyewood extracts, above referred to, were formerly of very great importance in woollen-printing, but since the introduction of the coal-tar colouring matters, they have become of less importance.

139. *Application to Silk.* — Stannous chloride is principally used in conjunction with Catechu in producing heavily weighted blacks, where, indeed, it is of prime importance; the mode of its use is given in treating of the applications of Catechu (*see* p. 371).

140. **Tin Spirits** is a general term given to solutions of tin, in the preparation of which other acids besides hydrochloric acid are used, *e.g.*, nitric acid and sulphuric acid. They are really solutions of very variable composition, and whose utility, under various conditions, must be determined empirically. Each bears a special name to denote its intended particular application. They are chiefly used in wool dyeing, but their former importance has been lost through the introduction of the coal-tar colours.

The following are those which consist of stannous salt:—

Yellow Spirit is the name given to a solution of tin in which the hydrochloric acid has been partly replaced by sulphuric acid. This preparation, used in conjunction with the yellow dyewoods, is said to yield purer yellows than pure stannous chloride. It is sometimes called "sulpho-muriate of tin."

Amaranth Spirit and *Plum Spirit* are both similar in character to Yellow spirit, although the name Plum spirit is also given to a solution of tin in a mixture of hydrochloric and nitric acids.

Scarlet Finishing Spirit is "muriate of tin" containing a certain proportion of oxalic acid and sometimes also tartaric acid. It is said to be useful in imparting brilliancy to cochineal scarlets if added to the dye-bath in small amount towards the end of the dyeing operation, the chief mordant used being "nitrate of tin."

Finishing Spirit is a name given to a simple solution of "muriate of tin," or one containing a small proportion of sulphuric acid. It is added to the dye-bath towards the end of the operation in dyeing Prussian Blues on wool for the purpose of imparting brilliancy to the colour.

141. Stannous Nitrate.—This mordant may be prepared by dissolving freshly precipitated hydrated stannous oxide $Sn(OH)_2$ in cold dilute nitric acid; in practice, however, the hydrated oxide is replaced by metallic tin, in which case the liquid contains ammonium nitrate:—

$$4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

The usual method is to gradually dissolve rods of tin in eight times their weight of cold nitric acid 32° Tw. (Sp. Gr. 1·16), taking care to avoid evolution of nitrogen dioxide. The nitric acid should also be free from the lower oxides of nitrogen.

As prepared by the dyer, it is a deep yellow solution of about 60° Tw. (Sp. Gr. 1·3), liable to decompose spontaneously and to deposit a white precipitate on long standing.

Although the real chemical composition of this solution seems to be still unsettled, it probably contains the tin essentially as a stannous salt, but metastannic salt is also present, as indicated by its amber colour.

It is known in the dyeing trade by the following names:—*Bowl spirit, scarlet spirit,* and *nitrate of tin.*

It is a very favourite mordant with woollen dyers for the production of cochineal scarlets, and this indeed is its principal use.

142. Stannic Chloride.—This mordant is prepared by leading chlorine gas into a solution of stannous chloride:

$$\underset{\substack{\text{Stannous}\\\text{chloride.}}}{SnCl_2\cdot 2H_2O} + Cl_2 + 3H_2O = \underset{\substack{\text{Stannic}\\\text{chloride.}}}{SnCl_4\cdot 5H_2O}$$

or by oxidising a solution of stannous chloride and hydrochloric acid, with nitric acid, chlorate of potash, or other oxidising agent:

$$3SnCl_2\cdot 2H_2O + \underset{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid.}}}{6HCl} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Stannic}\\\text{chloride.}}}{3SnCl_4} + 2NO + 10H_2O$$

$$3SnCl_2\cdot 2H_2O + 6HCl + \underset{\substack{\text{Potassium}\\\text{chlorate.}}}{KClO_3} = 3SnCl_4 + KCl + 9H_2O.$$

The method in which potassium chlorate is employed as the oxidising agent is one easily carried out, and it gives an excellent preparation. The stannous chloride is dissolved in the hydrochloric acid with or without the addition of a little water, and the solution is gently warmed, in order to ensure the beginning of the reaction. It is then only necessary to add, as rapidly as the reaction permits, small quantities of potassium chlorate until the calculated amount has been added. The necessary heat is maintained by the somewhat energetic action which takes place on each addition of potassium chlorate. The stannic chloride solution thus obtained should be colour less. With excess of potassium chlorate, it is yellow from the presence of free chlorine, and this may serve to indicate when the correct amount has been added. With a deficiency of hydrochloric acid the solution becomes turbid. The following proportions have been determined by experiment as suitable:—337 grams of tin crystals, 300 grams of hydrochloric acid, 24° Tw. (Sp. Gr. 1·12), 58 grams of potassium chlorate.

Several crystalline hydrates of stannic chloride have been recognised; the best known is the penta-hydrate ($SnCl_4 \cdot 5H_2O$), which is an article of commerce.

Dilute solutions of stannic chloride decompose spontaneously on long standing, but decomposition with precipitation of hydrated stannic oxide is at once effected on boiling:

$$SnCl_4 + 4H_2O = \underset{\text{Stannic hydrate.}}{Sn(OH)_4} + 4HCl.$$

143. Pink Salt.—This is a double salt of stannic chloride with ammonium chloride [$SnCl_4 \cdot 2(NH_4Cl)$]. When concentrated solutions of the two salts are mixed in the requisite proportions, it is deposited as a white crystalline powder. It dissolves in water without decomposition. A dilute solution is dissociated by heating, hydrated stannic oxide being precipitated.

Though formerly much used by the calico-printer, this mordant seems to be only rarely employed at present.

144. Tin Spirits.—Reference has already been made to certain solutions of stannous salts, which bear this name (*see* p. 198), but the name includes a still more numerous class in which stannic salts are present. The term "spirit" here used is derived from the antiquated names "Spirits of salt" and "Spirits of nitre" applied to hydrochloric acid and nitric acid respectively, since these are the essential solvents of the tin, although ammonium chloride and sodium chloride and other salts are sometimes introduced. "Tin spirits" are the result of pure empiricism, and their mode of manufacture was formerly a matter of profound secrecy among dyers. Since the introduction of the coal-tar colours their former importance has very considerably diminished. According to the particular use for which they seemed to be most suitable or at the fancy of the dyer, they received one or other of the following names: *Nitro-muriate of tin, tin composition, cotton spirits, barwood spirits, crimson spirits, purple spirits, physic, &c.*

It is useless to give a selection of receipts of these solutions, for they are endless, and no good purpose would be served by so doing. The following is a summary of the relative proportions of ingredients which have been used in practice:—

a. 100 grams of nitric acid 64° Tw. (Sp. Gr. 1·32).
150—600 grams of hydrochloric acid 32° Tw. (Sp. Gr. 1·16).
6—12 per cent. of the weight of mixed acids of tin.
In some cases even 30—40 per cent. of tin has been used.
b. 100 grams of nitric acid 64° Tw. (Sp. Gr. 1·32).
12·5 grams of ammonium chloride (or 5 grams NaCl).
12—16 per cent. (of the weight of nitric acid) of tin.

The solutions are frequently diluted with water to a moderate degree.

Oxymuriate of Tin and *Pink Cutting Liquor* are names given to a preparation belonging to the same class, and made by adding gradually and with continual stirring 125—150 grams of nitric acid 62° Tw. (Sp Gr. 1·31) to 100 grams of stannous chloride crystals, and diluting slightly with water. It is a white, somewhat milky solution.

According to the proportions of the different ingredients, the temperature, and the method of procedure adopted in making the above mordants, their composition will vary exceedingly, not only as to acidity and percentage of tin, but also as to the state of oxidation in which the tin is present.

Much difficulty is experienced in the manufacture of tin mordants by the dyer, because of the fact already alluded to, that two stannic oxides exist, namely, stannic acid and metastannic acid; the former is soluble in nitric acid; the latter is insoluble. Metastannic acid is invariably formed whenever tin is violently acted upon by nitric acid, either because the latter is too concentrated, or the temperature employed is too high. The formation of this body as an insoluble precipitate constitutes the so-called "firing" during the preparation of some of the above mordants, and must be rigorously avoided by adding the tin slowly in the form of rods, keeping the acids cool, and preventing the evolution of nitrogen dioxide, since it means a loss of tin and a diminution of the mordanting power of the solution. But even when this violent oxidation does not take place, soluble metastannic chloride or complex oxychlorides are frequently formed, and the presence or absence of these in any solution of stannous or stannic salts influences very much its behaviour in mordanting.

Application of Stannic Salts to the various Textile Fibres.

145. *Application to Cotton.*—In ordinary yarn and piece dyeing stannic chloride finds only a limited use.

As barwood-spirit and red-cotton-spirit, it is used in dyeing reds with Barwood and Peachwood.

The cotton is first well impregnated with a decoction of tannin matter, then worked and steeped in a dilute solution of the stannic salt and finally washed. It is occasionally used for clarets and browns, in the production of which Fustic, Logwood, and Peachwood are used together in the dye-bath.

Stannic chloride is more extensively used in mordanting the cotton-warp of mixed goods for producing light bright shades. After dyeing the wool, the material is worked in a decoction of tannin matter, and afterwards in a solution of the stannic salt at 4° Tw. (Sp. Gr. 1·02).

Formerly, when dyewood extracts were the colouring matters employed, it was the hydrated stannic oxide which constituted the real mordant, and this it was which combined with the colouring matters of Peachwood, Logwood, Flavin, Cochineal, &c., to produce crimson, claret, purple, and various light compound colours. The tannic acid of the tannin matter merely acted as the fixing agent for the stannic oxide.

At present, however, in cases where the basic coal-tar colours are employed, the *rôles* of the two substances are exchanged, and the stannic chloride must be considered as the fixing agent and the tannic acid as the mordant. Some dyers have given the name "aniline spirit" to the tin solution which they considered specially suitable for this purpose.

It is very probable that a stannic chloride, free from stannous salt, made as above described by means of potassium chlorate or nitric acid, would suit all cases where cotton has to be mordanted with tin and tannic acid. The presence of stannous salt is, as a rule, injurious, because of its reducing action, and because in the case of mixed goods of cotton and wool it is apt to mordant the latter.

146. *Application to Wool.*—Pure stannic chloride is not a suitable mordant for wool.

If wool is boiled with a dilute solution of pure stannic chloride, washed, and dyed with a polygenetic colouring matter—*e.g.*, Camwood, Logwood, &c.—it only acquires a useless stain, and the addition of a very large amount of cream of tartar to the mordanting bath is necessary before any good, full, useful colour can be thus obtained. It is no doubt this deficiency of mordanting power for wool under certain conditions, that renders stannic chloride such a useful mordant for cotton in the case of mixed goods of cotton and wool.

Notwithstanding this fact, many of the above-mentioned preparations containing stannic salt are used in woollen dyeing. The tin is, however, chiefly present as a stannous salt, and the stannic compound is only there in limited proportion, or possibly the tin is present as a sesqui-compound, that is, in an intermediate state of oxidation, which has been little studied. The principal use of such mordants has been in the dyeing of cochineal scarlets.

147. *Application to Silk.*—Some of the solutions of tin in mixtures of nitric and hydrochloric acid were formerly much used, in conjunction with Brazil-wood and Logwood, for the production of red and purple colours on silk, under the names of "crimson spirit" and "purple spirit." They were applied to the fibre before or simultaneously with the colouring matter. Since the introduction of the coal-tar colours these mordants are seldom used.

Stannic chloride, however, is frequently used at the present time for the purpose of weighting white, and light-shades of silk. The raw silk is steeped for some time in a cold solution of stannic chloride, then washed and passed through a cold dilute solution of sodium carbonate, and finally washed in water. After repeating these operations several times, the silk is boiled-off in the ordinary way. In this manner the silk may be made to gain 25 per cent. in weight. This weighting gives the silk a false feeling of substantiality, and is not without some injurious influence on many of the colours subsequently applied. If the solution is used at a concentration of 100° Tw., the silk begins to dissolve; it contracts very considerably even when the solution is only 50° Tw.

148. **Stannate of Soda.**—This salt is also known as "preparing salt." It is manufactured on a somewhat extensive scale by fusing together sodium hydrate, sodium nitrate, and tin, generally with the addition of common salt:

$$2Sn + \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{3NaOH} + \underset{\substack{\text{Sodium}\\\text{nitrate.}}}{NaNO_3} = \underset{\substack{\text{Stannate}\\\text{of soda.}}}{2SnO_3Na_2} + NH_3$$

Other modes of manufacture are also known. The commercial product has the form of irregular, fused-looking, white, hard lumps. It dissolves almost entirely in water if freshly made, but if kept for some time exposed to air and moisture, it decomposes, and leaves much white sediment on dissolving. It generally contains variable quantities of sodium carbonate and common salt; some varieties contain also arsenate of soda or tungstate of soda. These last additions are supposed to increase or improve its mordanting qualities, but this is extremely doubtful. Its chief value depends upon the amount of tin which it contains, and this is somewhat variable, ranging as it does from 8 to 20 per cent., according to price.

In stannate of soda, the stannic oxide plays the part of an acid. It is precipitated from its solution by the addition of a mineral acid, a reaction on which its method of application is founded.

149. *Application to Cotton.*—Stannate of soda is employed to mordant cotton with hydrated stannic oxide previous to printing with certain colours. The cotton is thoroughly impregnated with a solution of stannate of soda 4°—10° Tw. (Sp. Gr. 1·02—1·05), then passed rapidly through very dilute sulphuric acid, and at once washed.

Calico prepared in this manner is sometimes called "steam-prepared cloth," since it is intended that certain steam-colours shall be printed upon it, more particularly those containing a tin or aluminium mordant. The stannic oxide upon the cloth tends to saturate the acid mordants of the colour, so that the fabric is less corroded, and a larger quantity of basic salt is fixed on the fibre. If the printing colour contains an aluminium mordant, there is probably fixed on the fibre a basic alumina-stannic compound. The result of preparing the cloth with stannic oxide is that the colours are richer, brighter, and faster to washing than they otherwise would be.

150. *Application to Wool.*—The woollen-printer applies stannate of soda as a preparation for steam-colours in a manner similar to that just described. The woollen cloth is padded twice in a solution of stannate of soda 16° Tw. (Sp. Gr. 1·08), and passed for five minutes through a solution containing, per litre of water, 5 cubic centimetres of sulphuric acid 168° Tw. (Sp. Gr. 1·84), and 6·25 cubic centimetres of bleaching-powder solution 10° Tw. (Sp. Gr. 1·05). The cloth is then well washed

and dried. More regular results are obtained if, after padding the cloth in stannate of soda, it is passed through dilute sulphuric acid about 3° Tw. (Sp. Gr. 1·015), and then, after washing, through a solution containing about one-fifth the above quantities of sulphuric acid and bleaching powder solution, and is finally washed. In bleached wool the chlorine oxidises the sulphur dioxide retained by the fibre.

Stannate of soda is not used in preparing silk.

CHROMIUM MORDANTS.

151. Two classes of chromium salts have been hitherto used as mordants; first, those corresponding to chromic oxide (Cr_2O_3), and in which the chromium is, as it were, the basic element of the salt; and, secondly, those corresponding to chromium trioxide (CrO_3), which plays the part of an acid. But it must be well borne in mind that with the latter the real mordanting effect takes place only after reduction of the chromic acid to chromic oxide.

Although the chromium mordants are capable of yielding excellent results, both as regards beauty and fastness of colour, their use has been comparatively limited, more particularly in cotton dyeing, owing to the absence, till recently, of satisfactory methods of application.

The chromium trioxide salts are certainly analogous in constitution to those of aluminium and ferric oxide, but in many respects their behaviour towards the textile fibres is very different.

152. Potassium Dichromate (bichromate of potash). —This compound ($K_2Cr_2O_7$) serves as the point of departure for making other chromium mordants. It is manufactured on a large scale from chrome-iron ore. The ground roasted ore is mixed with potassium carbonate and lime. The mixture is heated for the purpose of oxidation in a reverberatory furnace, and the calcium chromate formed is dissolved out with water. Potassium sulphate is added to the solution, and the requisite amount of sulphuric acid is added to the solution of potassium chromate thus obtained, to convert the latter into the dichromate.

The commercial product has the form of well-defined orange-coloured crystals. In the unground state it is not usually subjected to adulteration.

It is a powerful oxidising agent, and on this account alone it is frequently employed by the textile colourist, although it serves also as an excellent mordant for wool.

153. *Application to Cotton.*—Bichromate of potash is used by the cotton-dyer and calico-printer in the production of chromate of lead yellow and orange. To produce the yellow, the cotton is impregnated with a soluble lead salt (nitrate or acetate), and, after precipitation of the lead on the fibre as oxide or sulphate (by means of ammonia, lime, or sodium sulphate), passed through a hot dilute solution of potassium dichromate. An orange colour is obtained by a subsequent rapid passage through boiling milk of lime, whereby the yellow lead chromate ($PbCrO_4$) is changed more or less into the red basic lead chromate, Pb_2CrO_5.

In the production of browns or other colours in which catechu is a constituent element, potassium dichromate is used solely because of its oxidising property. The cotton is impregnated with a decoction of catechu, and subsequently passed rapidly through a boiling solution of potassium dichromate. The essential action during this process is that the active principle of the catechu (catechin), which has been attracted by the cotton, is oxidised, rendered insoluble, and fixed, it is said, as brown japonic acid. There is, of course, necessarily a simultaneous deposition of chromic oxide on the fibre through the reduction of the chromic acid of the potassium dichromate, and this may serve as a mordant for dyeing subsequently with other colouring matters, to produce various shades of brown.

In dyeing aniline black (*see* p. 390), and in the development of printed steam-blues, the potassium dichromate is also employed because of its oxidising action.

In some cases, the oxidising nature of this salt is made use of for the purpose of destroying colour instead of developing it. It is employed, for example, by the calico-printer as a discharge for indigo-vat-blue.

A thickened solution of potassium chromate is printed upon the blue calico, which, after drying, is passed rapidly through a cold and moderately concentrated solution containing oxalic and sulphuric acid. The moment the printed parts containing the potassium chromate come in contact with the acid solution, *there* chromic acid is liberated, the blue is destroyed, and a white pattern on a blue ground is the result. By adding the potassium chromate to insoluble pigment colours (vermilion, chrome green, &c.), thickened with albumen, coloured discharge patterns are similarly produced.

154. *Application to Wool.* — Bichromate of potash serves as an excellent mordant in woollen dyeing. The wool is boiled for 1—1½ hour with a solution, containing 2—4 per cent. (of the weight of the material employed), of bichromate of potash. After washing well, the material is ready for the dye-bath.

One point to be well borne in mind by the dyer, since it may be the source of uneven dyeing occasionally, is that the wool in the mordanted state is sensitive to the action of light; whereas the unexposed mordanted wool has a yellowish colour, when exposed to light it becomes greenish, through reduction of the absorbed salt and deposition of chromic oxide. The important point is that the exposed and unexposed portions behave differently in the dye-bath. The unexposed part dyes more rapidly than the other, and acquires a somewhat darker and less brilliant tint. No doubt the action of light on wool mordanted with bichromate of potash is similar to that which it has upon a film of gelatin impregnated with the same salt. The gelatin is rendered insoluble in water—a fact which is made use of in the autotype process of photography. Although the slow dyeing of the exposed portions may be partly caused by the wool being rendered less absorbent, it is also probably due to the different behaviour in the dye-bath of the deposited chromic oxide as compared with that of the absorbed bichromate of potash.

With some colouring matters—*e.g.*, the yellow dye-woods—larger percentages of mordant than those given may be employed, and deeper colours thus obtained. This, however, is not to be recommended, both on account of the increased expense, and because the dyed colours are said to fade more quickly. With many colouring matters, the injurious effect of mordanting with a large amount of bichromate of potash is already apparent in the dye-bath, the material refusing, as it were, to be dyed, although the real cause is probably the oxidation and destruction of the colouring matter, by the excess of bichromate of potash absorbed by the wool. In such cases, the wool is said to be "over-chromed."

The mordanting power of bichromate of potash for wool is somewhat remarkable.

The striking feature in connection with this use of bichromate of potash is, that with only a comparatively small percentage of it, full deep colours can be obtained. The use of any other salt containing an equivalent amount of chromium does not yield to the fibre the real mordanting body (chromic oxide) so completely, and colours of equal intensity are not obtained. It is a mordant easy of application, very effective in its action, and one which leaves the wool with a soft feel. If oxidation of the wool does take place, it is very slight, and this is certainly only a secondary accompaniment not by any means the essential action which accounts for the striking character of the mordanting powers of bichromate of potash.

With many colouring matters, by the addition to the mordanting bath of a mineral acid—*e.g.*, H_2SO_4—just sufficient in amount to take up the potassium and liberate chromic acid, the mordanting power of bichromate of potash is slightly increased, and deeper colours are obtained. Mordanting with pure chromic acid gives similar results. In both cases the mordanted wool has a yellowish colour.

When organic acids or acid salts—*e.g.*, tartaric acid, cream of tartar, &c.—are used along with the bichromate of potash, there is production of a chromic salt (Cr_2O_3) in the mordanting bath, and the wool assumes a green colour through the deposition of chromic oxide. In this case, the colours obtained in dyeing, although possessing more brilliancy and differing in tint, are essentially the same as those obtained on the yellow-coloured wool.

The best explanation of what takes place when wool is boiled with bichromate of potash or chromic acid, is that these bodies are simply absorbed in a more or less unchanged state, since they are largely removed from freshly mordanted wool by mere washing in water. In the dye-bath they undoubtedly suffer decomposition; *there*, under the influence of the colouring matter, reduction to chromic oxide takes place, and the production and fixing of chromium lake are probably effected simultaneously. The lesser brilliancy of the colour obtained on the yellow mordanted wool is explained by the wool absorbing the impure oxidation products of the colouring matter, which of course cannot take place in the case of the green mordanted wool where only chromic oxide is present.

Chromium lakes are produced with the greatest ease, apart from the fibre, by merely mixing together cold solutions of colouring matter (*e.g.*, logwood liquor) and bichromate of potash, and allowing them to stand for some time. Precipitation at once takes place on heating. The reactions which occur in dyeing wool mordanted with bichromate of potash are probably strictly analogous.

In some cases, the mordanting of the wool with bichromate of potash takes place *after* boiling with a decoction of the colouring matter, *e.g.*, with Camwood and the allied woods. In the application of Catechu to wool, the essential action of the potassium dichromate is one of oxidation, and the same method is adopted.

155. *Application to Silk.*—Bichromate of potash is used in the production of catechu browns; the method being similar to that employed for obtaining the same colours on cotton (*see* p. 207). It is occasionally used also in a like manner with certain logwood blacks.

156. **Sodium Dichromate.**—This salt ($Na_2Cr_2O_7 \cdot 2H_2O$) has been introduced into commerce as a substitute for the more expensive potassium salt. It is sold both in the crystalline and in the dehydrated state. Being somewhat deliquescent, it requires to be kept closed up or in a dry atmosphere; its greater solubility gives it an advantage over the potassium salt in some cases, *e.g.*, in the printing of coloured discharges on indigo-vat-blue calico. If equally pure it may be capable of replacing the potassium salt in most of its applications, possibly in all.

157. **Barium Chromate** ($BaCrO_4$) is an insoluble yellow precipitate, which has been used as a pigment by the calico-printer under the name of "yellow ultramarine." Its chief recommendation is that it does not blacken when subjected to the influence of sulphuretted hydrogen.

158. **Lead Chromate** ($PbCrO_4$) is a yellow precipitate known by the name of "chrome yellow." It is frequently used as a pigment by the calico-printer, but, unfortunately, it is blackened by sulphuretted hydrogen.

Mixtures of $PbCrO_4$ with the red basic compound Pb_2CrO_5 constitute the pigment "chrome-orange" of the calico-printer.

159. **Copper Chromate.**—When a solution containing copper sulphate and potassium dichromate is boiled, a basic salt ($Cu_3CrO_6 \cdot 2H_2O$) is thrown down as a brown precipitate. Such a solution has been employed for mordanting wool with good results.

160. **Chrome-Alum** (*Potassium chromium sulphate*).—This substance $\left[\begin{matrix}K_2\\Cr_2\end{matrix}\right\}(SO_4)_4 \cdot 24H_2O]$, though containing no aluminium is so called because its crystalline form

and chemical constitution are similar to those of ordinary alum. It is obtained in large quantities as a by-product in the manufacture of artificial Alizarin from anthracene, in which case it contains calcium sulphate and organic matter as impurities. If necessary, it may be specially prepared by adding to a solution of bichromate of potash containing the requisite quantity of sulphuric acid, any substances readily oxidised, *e.g.*, sulphurous acid, oxalic acid, alcohol, sugar, starch, glycerine, &c. The following equation represents generally the reaction which takes place:—

$$\underset{\substack{\text{Potassium}\\\text{dichromate.}}}{K_2Cr_2O_7} + 4\,(H_2SO_4) + 17H_2O + 3H_2 = \underset{\text{Chrome alum.}}{\left[\left.\begin{matrix}K_2\\Cr_2\end{matrix}\right\}(SO_4)_4{\cdot}24H_2O\right]}$$

The organic substances mentioned are added as rapidly as the violent reaction and effervescence will permit. The mixture becomes much heated, and care should always be taken not to allow it to cool, otherwise there is a possibility of the reaction ceasing, and external heat would then have to be applied.

The following proportions of ingredients are employed by calico-printers: 100 grams of $K_2Cr_2O_7$, 220 grams of water, 123 grams of H_2SO_4, 168° Tw. (Sp. Gr. 1·84), 24 grams of starch. When properly made, the solution should have a bluish-green colour; if olive-green, it still contains undecomposed bichromate of potash. Since the liquid has been heated, crystallisation takes place with difficulty; but, as a rule, after standing for a lengthened period, it deposits dark purple crystals. These dissolve in cold water, with a dirty bluish-violet colour, but if the solution be heated above 70° C., it acquires a green colour. On long standing the original colour returns.

The violet solution contains the normal salt, whereas the green solution is said to contain a mixture of basic and acid salts. This explanation is simpler and better than that which supposes the existence of two modifications of chromium hydrate.

These violet and green solutions differ from each other in many of their reactions, *e.g.*, barium chloride does not precipitate the whole of the sulphuric acid from the green solution at the ordinary temperature, whereas with the violet solution the decomposition is normal; ammonia precipitates hydrated chromic oxide, $Cr_2(OH)_6$, from both solutions, but only that obtained from the violet solution is soluble in excess of ammonia. Similar differences are shown by other chromic salts.

A normal chrome-alum solution is not decomposed either by heating or by dilution.

By adding calculated amounts of an alkaline carbonate or chromium hydrate to a solution of the normal chrome-alum, solutions containing basic chromium sulphates are obtained, for example, such as are represented by the following formulæ :—

$$Cr_2(SO_4)_2(OH)_2,\ Cr_4(SO_4)_3(OH)_6,\ Cr_2(SO_4)(OH)_4.$$

Such solutions will, of course, contain also potassium and sodium sulphate. Unlike those of the corresponding aluminium compounds, they show no sign of dissociation on heating (Liechti and Suida).

Dissociation by dilution is accelerated the more basic the salt is, *e.g.*, a solution containing $Cr_2(SO_4)_2(OH)_2$ must be diluted 85-fold before precipitation ensues, whereas $Cr_2(SO_4)(OH)_4$ requires only 1·5-fold dilution; but in all cases the precipitation is not complete. The presence of sodium sulphate makes the solution less sensitive to dissociation by dilution. Parallel with these facts are those which refer to the behaviour of chrome-alum solutions to the fibre; with increase of basicity a larger amount of chromic oxide is deposited on the fibre by the operations of impregnation, drying, and ageing. A solution of *normal* chrome-alum containing 224·6 grams per litre (*i.e.*, an amount equivalent to 150 grams of aluminium sulphate per litre) deposits on the cotton fibre

1·8 per cent. of the chromic oxide presented to it, an equivalent solution of the *basic* chrome-alum containing $Cr_2SO_4(OH)_4$ (made from chrome-alum and sodium carbonate) gives up 87·5 per cent. of the available chromic oxide. The presence of sodium sulphate in the solution hinders this deposition of mordant considerably.

A solution of chrome-alum is precipitated on the addition of sodium hydrate or ammonia, but the precipitate redissolves in an excess of the precipitant. The alkaline solutions thus obtained are precipitated on boiling. The precipitates caused by sodium carbonate, phosphate, and silicate are not redissolved in excess.

The basic salt $Cr_4(SO_4)_3(OH)_6$ behaves towards these reagents in a similar manner. It is remarkable that some of the basic sulphates are precipitated on the addition of acetic acid or sodium acetate.

The most basic salt solution obtainable by neutralising chrome-alum with sodium carbonate contains $Cr_2SO_4(OH)_4$, thus:

$$\underset{\text{Chrome-alum.}}{[K_2Cr_2(SO_4)_4\cdot 24H_2O]} + \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{2Na_2CO_3} + 2H_2O = \underset{\substack{\text{Basic}\\ \text{chromium sulphate.}}}{Cr_2SO_4(OH)_4} + K_2SO_4 + 2Na_2SO_4 + 2CO_2 + 24H_2O.$$

The presence of sodium sulphate makes the solution less sensitive to dissociation by dilution. This retarding influence is already seen from the fact that the most basic salt obtainable by neutralising chrome-alum with sodium carbonate is $Cr_2SO_4(OH)_4$, while if the chrome-alum is neutralised by adding chromic hydrate, the most basic salt obtainable is $Cr_4(SO_4)_3(OH)_6$ (Liechti and Suida).

161. **Chromium Sulphate** $[Cr_2(SO_4)_3]$ may be prepared by dissolving hydrated chromic oxide in sulphuric acid. Violet and green solutions exist. Basic salts are prepared by neutralising solutions of the normal salt with chromic hydrate or sodium carbonate. The most basic salt which can be prepared by the latter means is $Cr_4(SO_4)_3(OH)_6$

which decomposes spontaneously after standing for three months.

$$\underset{\substack{\text{Normal}\\\text{chromium}\\\text{sulphate.}}}{2Cr_2(SO_4)_3} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{3Na_2CO_3} + 3H_2O = \underset{\substack{\text{Basic}\\\text{chromium sulphate.}}}{Cr_4(SO_4)_3(OH)_6} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{3Na_2SO_4} + 3CO_2.$$

With the use of chromic hydrate, the most basic salt obtainable is $Cr_2(SO_4)_2(OH)_2$, thus:

$$2Cr_2(SO_4)_3 + \underset{\substack{\text{Chromic}\\\text{hydrate.}}}{Cr_2(OH)_6} = \underset{\substack{\text{Basic}\\\text{chromium sulphate.}}}{3Cr_2(SO_4)_2(OH_2)}.$$

In the first case the neutralising can be pushed to a further limit because *there* the presence of the sodium sulphate tends to retard the dissociation of the basic salt. Neither of these is so basic as the solutions similarly obtained from chrome-alum. Both the normal and the basic chromium sulphates behave in respect of dissociation by heating and by dilution, like the corresponding chrome-alum solutions; the same may be said of their behaviour with sodium hydrate, ammonia, sodium carbonate, phosphate, and silicate.

A solution of normal chromium sulphate (equivalent to 224·6 grams of chrome-alum per litre) deposits 12·8 per cent. of the available Cr_2O_3 on the cotton fibre by the operations of impregnation, drying, and ageing; an equivalent solution of the basic salt $Cr_4(SO_4)_3(OH)_6$ made from chromium sulphate and sodium carbonate yields to the fibre 86·4 per cent. of the available chromic oxide. Although these solutions of pure chromium sulphate cannot be made as basic as those of chrome-alum, they give up practically the same amount of chromium oxide to the fibre under the above conditions, because they are more sensitive (Liechti and Suida).

162. **Chromium Acetate.**—A solution of the normal salt $[Cr_2(C_2H_3O_2)_6]$ may be prepared by mixing, in suitable proportions, solutions of lead acetate and chromium

sulphate or chrome-alum; in the latter case, of course, potassium sulphate is present.

$$\underset{\text{Chrome alum.}}{\left[\begin{matrix}K_2\\ Cr_2\end{matrix}\right\}(SO_4)_4\cdot 24H_2O]} + 3[\underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2\cdot 3H_2O}] = \underset{\text{Chromium acetate.}}{Cr_2(C_2H_3O_2)_6}$$

$$+ 3PbSO_4 + K_2SO_4 + 33H_2O.$$

It is both interesting and remarkable that a solution of normal chromium acetate, prepared as above indicated, is not dissociated on boiling, however much diluted the solution may be. It is not precipitated in the *cold* by caustic alkalis, alkaline carbonates, phosphates, and silicates, ammoniacal soap, or sulphated-oil solutions, but on *boiling* with these additions, complete precipitation is effected. The duration of the boiling necessary to cause decomposition varies with the amount of dilution, and if the addition made be phosphate of soda, very long boiling is required (Liechti and Suida).

A solution of pure chromium acetate can be evaporated to dryness, and be even heated to 230° C., it is said, without losing its solubility.

If a freshly prepared violet solution of normal chromium acetate be boiled, it becomes greenish-violet, and if basic salts are made from this by the addition of sodium carbonate, they soon decompose. A similar change takes place if a solution of the normal salt is kept for a long time; it loses its violet colour, and is then readily precipitated by sodium carbonate on heating. Somewhat less sensitive basic mordants are obtained, if the sodium carbonate is added in two portions, and the liquid is gently heated after the first addition.

On the contrary, if from a *freshly* prepared violet solution of normal chromium acetate, basic solutions are made by adding sodium carbonate, such solutions retain the violet colour; they may be kept for a long time, and may even be heated gradually to the boiling point without undergoing decomposition. If, however, after long keeping, a very slight further addition of sodium carbonate is made, complete decomposition takes place at once on boiling the solution.

Solutions of basic acetates may be obtained by making suitable additions of an alkaline carbonate to solutions of the normal salt, or by adding lead acetate to solutions of basic chromium sulphates. It is possible even to make a solution so basic that it contains three molecules of sodium carbonate to one of chromium acetate.

It is an interesting fact that the more basic a chromium acetate is, the more lead sulphate it can hold in solution. On the addition of acetic acid it is precipitated. The presence of sodium acetate also causes lead sulphate to be dissolved, but in this case an addition of acetic acid does not precipitate it (Liechti and Suida).

The basic chromium acetates are not dissociated by dilution, and only the most basic dissociate on heating; a solution, for example, of the basic salt $Cr_2(C_2H_3O_2)_4(OH)_2$ (made from basic chromium sulphate and lead acetate, and equivalent to 224·6 grams of chrome-alum per litre) is not dissociated on heating, unless it be diluted 75-fold. It yields to the cotton fibre by the operations of impregnation, drying and ageing, 29·5 per cent. of the available chromic oxide. The more basic salt $Cr_2(C_2H_3O_2)_3(OH)_3$ made in the same way, dissociates when heated to 80°—90° C., and gives up to the cotton fibre 66 per cent. of the chromic oxide presented to it. An equivalent solution of *normal* chromium acetate yields only 8·4 per cent. of the available chromic oxide to the fibre when similarly applied.

163. **Chromium Sulphate-Acetate.**—Solutions of these are prepared by adding to a solution of chrome-alum such amounts of lead acetate as are insufficient to cause complete decomposition. They bear, to a certain extent, the character of solutions of chromium acetate, not being affected in the cold by the ordinary precipitants, but only on heating. Basic salts are made in the same way, substituting basic chromium sulphates for chrome-alum. Only the most basic show signs of dissociation on heating or diluting.

164. Chromium Nitrate and Chromium Chloride are prepared by the double decomposition of solutions of chrome-alum with lead nitrate and barium chloride respectively.

Solutions of basic salts are prepared by making suitable additions of an alkaline carbonate. These solutions, on diluting and heating, behave very similarly to the corresponding solutions of chromium sulphate, *i.e.*, they are not readily dissociated. The nitrate seems to be the most susceptible, and the sulphate the least, while the chloride holds an intermediate place.

165. Chromium Nitrate-Acetate.—Solutions of this salt may be made by mixing together solutions of chrome-alum or chromium sulphate, lead nitrate, and lead acetate.

$$Cr_2(SO_4)_3 + \underset{\text{Lead nitrate.}}{Pb(NO_3)_2} + \underset{\text{Lead acetate.}}{2[Pb(C_2H_3O_2)_2\cdot 3H_2O]} =$$

$$= \underset{\substack{\text{Normal}\\ \text{chromium nitrate-acetate.}}}{Cr_2(NO_3)_2(C_2H_3O_2)_4} + 3PbSO_4 + 6H_2O.$$

Basic salts are prepared by adding sodium carbonate to solutions of the normal salt.

A very suitable method of preparing solutions of basic salt is to reduce bichromate of potash with glycerine, the requisite amounts of nitric and acetic acid being also added, thus:

$$2K_2Cr_2O_7 + 6HNO_3 + \underset{\text{Acetic acid.}}{4C_2H_4O_2} + 6H_2 = 4KNO_3 +$$

$$+ \underset{\substack{\text{Basic}\\ \text{chromium nitrate-acetate.}}}{2Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3} + 8H_2O.$$

Dissolve 100 grams of bichromate of potash in 150 grams of warm water, then add 131 grams of nitric acid, 64° Tw. (Sp. Gr. 1·32); cool the solution a little, and add gradually a mixture of 29 grams of glycerine and 134 grams of acetic acid, 10° Tw. (Sp. Gr. 1·05). The solution obtained may be evaporated a little and cooled, in order to allow the potassium nitrate to crystallise out.

166. Chromium Thiocyanate.—A solution of the normal salt $Cr_2(CNS)_6$ is prepared by mixing together solutions of normal chromium sulphate and barium thiocyanate. With solutions of sodium hydrate, ammonia, sodium carbonate, and phosphate, it behaves very like a chrome-alum solution. Basic salts are prepared by adding sodium carbonate to a solution of the normal salt. The most basic salt $Cr_2(CNS)(OH)_5$ decomposes after a few hours' standing, but the rest are quite stable.

The chromium thiocyanate solutions are not dissociated either by boiling or by dilution; if, however, diluted excessively, and then boiled or allowed to stand for a long time, some of the more basic salts dissociate.

A solution of the basic salt $Cr_2(CNS)_2(OH)_4$ (equivalent to 224·6 grams of chrome-alum per litre) gives up 33·6 per cent. of the available chromic oxide to the cotton fibre by the operations of impregnation, drying, and ageing. In this respect chromium thiocyanate is much behind chrome-alum and chromium sulphate.

167. **Alkaline Chromium Mordants.**—In considering the previous mordants, it has been stated that sodium hydrate, and ammonia precipitate their solutions, and that an excess of the precipitant redissolves in the cold the precipitate at first formed. Chromium hydrate may also be precipitated from a solution of chrome alum by sodium carbonate, then washed and dissolved in a cold concentrated solution of caustic soda. Such alkaline solutions of chromic hydrate are prone to decompose spontaneously, but the more alkaline the solutions, the less liable they are to do this, and it is quite possible to use them for the purpose of mordanting cotton.

168. *Application of the Chromium Salts to Cotton.*—The great importance of chromic oxide as a mordant for cotton, and the stability of its lakes, have long been recognised, but until recently no very satisfactory methods of fixing it simply, and in sufficient quantity upon the fibre, were recognised.

Chromium nitrate, sulphate, nitrate-acetate, and acetate have been much used by the calico-printer for steam-colours, *e.g.*, for blacks, browns, olives, &c., the colouring matters used in conjunction with them being, as a rule, decoctions of Logwood, Quercitron Bark, Sapanwood, Alizarin, &c.

The method of impregnating the cotton with the chromium solution and steaming seemed indeed as if it might be the only method of fixing an adequate amount of mordant on the fibre for purposes of dyeing, since the ordinary methods of precipitation employed with the aluminium and iron mordants give only very indifferent results.

Satisfactory results are, however, obtained by adopting the method proposed by H. Köchlin. The cotton is impregnated with the chromium solution, dried, and then passed through a boiling solution of carbonate of soda (100 grams per litre). Solutions of the basic sulphate, $Cr_4(SO_4)_3(OH)_6$, and the basic nitrate, $Cr_2(NO_2)_3(OH)_3$, give the best result; then follows the basic nitrate-acetate, $Cr_2NO_3(C_2H_3O_2)_2(OH)_3$; but *all* the chromium salts, even the normal ones, allow a satisfactory amount of mordant to be precipitated upon the fibre by this method. If the temperature of the soda solution is below the boiling point, or if phosphate of soda, &c., be substituted for the carbonate, the results obtained on dyeing are not so good. With regard to this last point, it is quite possible that the difference may be caused through the precipitated chromic phosphate not possessing such a power of attracting colouring matter as hydrated chromic oxide.

If the cotton before being impregnated with the chromium solution is prepared with ammoniacal sulphated oil (100 grams per litre), the results obtained on dyeing are still further improved. In this case ground chalk suspended in water may be substituted for the soda solution, and with equally good results.

Liechti and Schur have shown that a solution of chromium acetate or nitrate-acetate, is not precipitated by addition of an alkali in the cold, but only on heating, and point out that this fact is capable of being applied by the calico-printer for steam-colours. The printing-colour may be made by mixing in the cold, suitable proportions of chromium nitrate-acetate, sodium carbonate, and colouring matter. Good results are obtained, for example, with such colouring matters as Logwood extract and Alizarin, the chief difficulty being apparently that the mixture is apt to decompose and become gelatinous on standing.

The following are the proportions of ingredients of a steam-alizarin-chocolate mixture given by Liechti and Schur :—

100 cubic centimetres of basic chromium-nitrate-acetate 58° Tw. (Sp. Gr. 1·29).
250 grams of alizarin (10 per cent. paste).
25 ,, ammonia (20 per cent.).
11 ,, sodium carbonate crystals.

Make up to one litre with water.

More recently H. Kŏchlin has observed that cellulose possesses the property of attracting chromic oxide by mere steeping for several hours in an alkaline solution of chromium acetate. The following is the solution recommended : 100 grams of chromium acetate, 23° Tw. (Sp. Gr. 1·115), 100 grams of caustic soda, 66° Tw. (Sp. Gr. 1·33), 50 grams of water. Cotton may be mordanted by steeping in this solution for twelve hours ; after washing it is ready for dyeing. In practice, however, the method of drying, quick steaming, and washing, is preferred. The chromic oxide fixed on the cotton is said to be still combined with soda, forming, as it were, an acid chromite of soda.

Another method adopted by the calico-printer, but capable of wider application, is to print or pad the calico in a solution containing potassium dichromate, sodium thiosulphate, and magnesium acetate. At the ordinary temperature, and without access of light, these various salts do not react upon each other, but if the printed or padded cloth, after drying, is steamed, under the influence of the magnesium acetate, reduction of the potassium dichromate by the thiosulphate takes place, and chromic oxide is deposited upon the fibre.

169. *Application to Wool.*—The only chromium salt (other than bichromate of potash) which seems to have been used as a mordant for wool is chrome-alum. It is capable of giving good results, but it requires the addition of somewhat large amounts of cream of tartar to the mordanting bath, in order to render the latter properly effective. In any case its mordanting power is by no means equal to that of an equivalent quantity of bichromate of potash.

In those cases where the oxidising action of bichromate of potash acts injuriously upon the colouring matter employed, the use of chrome-alum in its stead might certainly be recommended, but for the great majority of cases it has no advantages over its more successful rival.

It is possible that some of the basic salts of chromium may mordant wool better than the normal ones, but it will be difficult for them to supplant bichromate of potash.

170. *Application to Silk.*—The chromium salts in which the chromium acts as a base have hitherto found little or no use in silk dyeing. They are, however, well worth the attention of the dyer.

COPPER MORDANTS.

The use of copper salts as mordants is unimportant; in most of the cases where they are employed by the textile colourist, they serve principally as oxidising agents.

171. **Copper Sulphate** ($CuSO_4 \cdot 5H_2O$) is manufactured in large quantities by roasting copper pyrites or other ores containing copper, and subsequently heating them with sulphuric acid. Purification from iron is generally effected by first precipitating the whole of the copper from the impure solutions by means of iron, and then re-dissolving it in dilute sulphuric acid. To the dyer, copper sulphate is well known under the names "blue-vitriol," "blue-stone," &c.

Several insoluble basic sulphates are known.

172. Copper Nitrate [$Cu(NO_3)_2 \cdot 3H_2O$] is obtained in solution by dissolving copper or copper oxide in nitric acid, or by the double decomposition of solutions of copper sulphate and lead nitrate. On evaporating the solution deliquescent crystals are obtained. In the dry state it is of a very unstable nature, and possesses strong oxidising properties.

173. Cupric Chloride ($CuCl_2 \cdot 2H_2O$) is obtained in solution by dissolving copper oxide or carbonate in hydrochloric acid. In the crystalline state it is very deliquescent. Insoluble basic cupric chlorides are known.

174. Copper Acetate.—The normal salt having the formula [$Cu(C_2H_3O_2)_2.H_2O$] is obtained in solution by dissolving hydrated copper oxide or carbonate in acetic acid, or by the double decomposition of copper sulphate and lead acetate solutions. In the crystalline state it effloresces when exposed to the air. It is very soluble in water. Of basic copper acetates the best known is "blue verdigris" [$Cu_2O(C_2H_3O_2)_2 \cdot 6H_2O$].

175. Copper Sulphide (CuS) is obtained as a black precipitate by the double decomposition of copper sulphate and sodium sulphide solutions.

176. *Application of the Copper Salts to Cotton.*—All the above copper salts are used on account of their oxidising properties. In this respect the nitrate is the most energetic. They enter, for example, into the composition of several calico-printing colours containing Catechu, *e.g.*, madder browns; also in steam-colours containing colouring principles whose colouring power is developed by oxidation, *e.g.*, decoctions of Logwood, Sapanwood, &c. Copper sulphate and nitrate have also been used in printing-colours intended to resist the fixing of indigo-vat-blue on calico, in which case they oxidise and precipitate the indigo before the reduced indigo solution can reach the fibre.

The cotton dyer frequently adds copper sulphate in small quantity to the catechu decoction used for producing catechu browns (*see* p. 369), and it is occasionally employed as an oxidising agent in the production of certain logwood blacks.

Copper sulphide forms a usual constituent of the aniline black printing-colour of the calico-printer. During the ageing process it is changed into copper sulphate, which assists in the oxidation of the aniline salt.

177. *Application to Wool.*—Copper sulphate may be used as a veritable mordant in wool-dyeing, and be applied after the boiling of the wool with the colouring matter as a so-called "saddening" agent. Very often it is used in this manner along with ferrous sulphate. In conjunction with cream of tartar, it may certainly be applied in the ordinary manner, *i.e.*, previous to boiling with the solution of colouring matter, but the colours thus produced possess no superiority over those obtained by the use of other cheaper mordants, *e.g.*, bichromate of potash.

178. *Application to Silk.*—Copper salts were formerly used in conjunction with Logwood for obtaining imitation indigo blues. At present they are occasionally used as "saddening" agents, and to give a particular tone of colour to certain blacks.

LEAD MORDANTS.

179. **Lead Acetate** [$Pb(C_2H_3O_2)_2 \cdot 3H_2O$], known also as "white sugar of lead," is prepared by dissolving the requisite amount of litharge (PbO) in acetic acid, and evaporating the solution to crystallisation. "Brown sugar of lead" is prepared in the same way, substituting crude acetic acid or pyroligneous acid for the purer acid.

A solution of the basic lead acetate, $(C_2H_3O_2)_2Pb_2O \cdot H_2O$, is obtained by dissolving the calculated amount of litharge in a solution of the normal acetate. By using excess of litharge, a still more basic solution is obtained. Both solutions soon become milky through absorption of carbonic acid from the air.

180. **Lead Nitrate** [$Pb(NO_3)_2$] is prepared in a similar manner by dissolving litharge in hot dilute nitric acid. It frequently contains copper as an impurity. A solution

of basic nitrate of lead [$Pb(NO_3)(OH)$] is obtained by boiling a solution of the normal salt with the calculated amount of litharge.

Application of lead salts to the fibres.—The above salts are used both by the calico-printer and the cotton-dyer for the production of orange and yellow colours. The cotton is printed or impregnated with a solution of the lead salt, and afterwards passed into a solution of bichromate of potash. With the calico-printer, steaming of the dried printed fabric and fixing of the lead as lead sulphate, by means of sodium sulphate, may intervene; with the cotton-dyer these operations are replaced by passing the cotton impregnated with lead salt into a bath containing milk of lime or ammonia. In the colour produced, the lead oxide fixed on the fibre may fairly be considered to act as the mordant, and the bichromate of potash, or chromic acid, as the colouring matter.

Basic lead acetate is used for the weighting of white silk.

The great defect of lead colours is that they are poisonous, and are blackened when exposed to the action of sulphuretted hydrogen.

MANGANESE MORDANTS.

Although hydrated manganese oxides may act as mordants, manganese salts have not hitherto been employed by the dyer for this purpose.

181. **Manganous Chloride** [$MnCl_2 \cdot 4H_2O$,] obtained as a by-product when dissolving manganese dioxide in hydrochloric acid for the production of chlorine, is used in dyeing cotton manganese brown or bronze. The cotton is impregnated with a solution of manganous chloride, then submitted to the action of ammonia or passed through a boiling solution of caustic soda, and the manganous hydrate thus precipitated is oxidised to form brown manganic hydrate either by exposing the cotton to air or by passing it through a dilute solution of bleach-

ing-powder. Cotton thus dyed brown may be further treated with solutions of various aromatic amines, *e.g.*, sulphates of aniline, naphthylamine, &c., for the production of fast aniline black, naphthylamine brown, &c. In this case the manganic oxide acts, not as a mordant, but as an oxidising agent towards the organic salts.

182. Potassium Permanganate [$KMnO_4$] is prepared by heating a mixture of manganese dioxide, potassium chlorate and caustic potash, and extracting the sintered mass with water. On account of its powerful oxidising properties, it has been proposed as a bleaching-agent for cotton, wool, and silk. Its application in this direction has, however, met with little success.

SULPHUR AS A MORDANT.

183. It has been observed by Lauth that when wool is boiled with a solution of thiosulphate of soda ($Na_2S_2O_3 \cdot 5H_2O$) (generally called hyposulphite of soda), to which a mineral acid has been added, the fibre undergoes a peculiar change. It loses its elasticity, and becomes soft and contracted. Amorphous sulphur is, indeed, precipitated upon the fibre, and thus imparts to it a special attraction for certain basic coal-tar colouring matters. This property has been made use of in practice in dyeing with Methyl and Malachite Greens, for which (more particularly the former) wool has little affinity. Experiment proves that only that modification of sulphur which is insoluble in carbon disulphide can act as a mordant in this way.

SILICA AS A MORDANT.

184. It has been observed that if cotton or wool be impregnated with a solution of silicate of soda, and then passed into dilute mineral acid, so as to precipitate silica upon the fibre, they dye up very well in solutions of certain coal-tar colouring matters, for which they have naturally little or no attraction. It has been found, too, that precipitated silica has the power of attracting alumina and other mordants, and can then be dyed much in the same way as mordanted cotton can.

TANNIC ACID AS A MORDANT AND AS A FIXING-AGENT FOR MORDANTS.

185. **Tannic Acid** is the name given to a certain astringent principle found in Gall-nuts, Sumach, Myrabolams, and other vegetable products, which are largely used by the textile colourist.

It is readily extracted from the above substances by means of a mixture of alcohol and ether. In its pure state, it appears as an amorphous, colourless powder, very soluble in water, and possessing a strong astringent taste and an acid character.

Its employment by the dyer depends upon the following properties :—

1. Towards colouring matters of a basic character—*e.g.*, Magenta, Malachite Green, &c.—tannic acid acts the part of a mordant, as truly as alumina does towards such phenolic colouring matters as Alizarin, since it combines with the colourless base they contain, to produce an insoluble coloured lake or pigment. During the precipitation of the solution of a basic colouring matter by tannic acid, there is always a liberation of the hydrochloric acid or other acid in combination with the colour-base. J. Köchlin has noticed, for example, that the addition of an alkali—*e.g.*, carbonate of soda—to the mixture, facilitates the precipitation and renders it more complete. For the production of a tannic acid lake, it is not at all essential that the tannic acid should be in the free state. Insoluble metallic tannates possess an equal, if not greater, attraction for basic colouring matters. The presence of the metallic oxide facilitates the decomposition by reason of a portion neutralising the liberated acid of the colouring matter, and it is probable that a very insoluble dibasic compound (tannate of antimony and colour-base) is produced. The use of an insoluble metallic tannate prevents the colour-lake formed on the

fibre from being re-dissolved during the process of dyeing or of final washing, either by excess of tannic acid or colouring matter. It is well known that excess of tannic acid gives soluble compounds with basic colouring matters, a fact which makes it necessary to apply to the cotton fibre, first the exact amount of tannic acid requisite, and then the colouring matter.

2. Just as tannic acid can produce insoluble compounds with *organic* colour-bases, so it does with *inorganic* bases, *e.g.*, alumina, ferric oxide, stannic oxide, &c. These bases act, as we know, as mordants for colouring matters of an acid character (Alizarin, &c.), and whether they be in the form of hydrates or combined with tannic acid (or other acids, *e.g.*, phosphoric, arsenic acid, &c.), they still have the power of attracting such colouring matters to produce coloured lakes. It is on this account that tannic acid is frequently employed as a precipitant, or "fixing agent," for such mordants as those of aluminium, tin, and iron.

3. The tannic acid compound, obtained with the iron mordants, possesses a bluish-black colour, sufficiently intense in itself to serve as a grey, or even black, dye. In this particular connection, tannic acid might certainly be considered as a true colouring principle, in the same sense as Alizarin. In many cases, however, the bluish-black tannate of iron serves merely to darken or intensify the colour obtained by the use of some other specially applied colouring matter, fixed either by reason of the tannic acid or the ferric oxide, and in such cases, one may say, that the tannate of iron plays the double part of mordant and ground-colour.

Some of the fibres possess a considerable power of attracting tannic acid from its solutions without the aid of any intermediary substance. The amount of tannic acid thus fixed by the cotton fibre depends largely upon the concentration of the solution employed, and, indeed, cotton well charged with tannic acid, by steeping in a strong solution, will give up a portion of the tannic acid if steeped in an excessively dilute solution, or even the whole of it if immersed in a current of pure water. The attractive power of the cotton, however, is much stronger than the solvent power of the water; according to J. Köchlin, cotton impregnated with tannic acid, by steeping in a solution containing 50 grams per litre, will even gain additional tannin if steeped in a solution containing 20 grams per litre. It will even retain the whole of its tannic acid in a solution containing as little as 5 grams per litre, and will only begin to lose tannic acid in a solution containing 2 grams per litre. It is evident from this last fact that it is not possible to exhaust a tannic acid bath—a fact which has analogies in dyeing the woollen fibre with some coal-tar colouring matters. Cotton attracts tannic acid less readily from an alcoholic or acetic acid solution than from water.

186. *Application to Cotton.*—To the cotton-dyer and calico-printer, tannic acid is one of the most useful substances, whether it be employed in the form of the vegetable products containing it or in a technically pure state.

There are two methods of preparing cotton with tannic acid. The first consists in working or *steeping* the cotton in a tannic acid solution for a comparatively *long period*—the duration varying with the concentration of the solution—and then removing the excess of liquid by squeezing or wringing, this being succeeded in some cases by drying. The second method is that of *padding*, which consists in simple impregnation with the solution for *a few seconds*, then squeezing and drying; in which case, the solutions employed must contain, at least, ten times as much tannic acid as those in the first method, to be equally effective.

In both methods it is advantageous to fix the tannic acid on the fibre as an insoluble compound, so that the prepared cotton will bear washing in water without any of the tannic acid dissolving off then or in any subsequent bath.

The drying, and even subsequent steaming, of tannin-prepared cotton, which is sometimes adopted, does not fix the tannic acid in such a manner as to prevent its being abstracted by water; after these operations, the cotton is simply in a more suitable state for passing into the fixing bath, since the latter is then less liable to be contaminated with tannic acid dissolved from the cotton, and stronger colours also are subsequently obtained.

In the *steeping* method, the absorption of tannic acid by the cotton is somewhat slow, and it cannot be accelerated by raising the temperature of the solution beyond 50° — 60° C. At and beyond this temperature, the cotton even loses some of the tannic acid which it takes up at lower temperatures. The duration of steeping can be diminished, however, by employing stronger solutions. In practice, it is usual to immerse the cotton in a hot solution, and to prolong the steeping, when possible, during twelve to twenty-four hours, or even more, until the liquid becomes cold. The initial heating of the solution, in this case, may have the beneficial effect of driving out the air from the interstices of the cotton, thus permitting its more equal and thorough penetration by the liquid.

The steeping method is adopted by the cotton-yarn dyer. If basic coal-tar colours are to be subsequently applied, the tannin is fixed on the cotton by working the latter for half an hour or more in a cold bath of stannic chloride, 4°—8° Tw. (Sp. Gr. 1·02—1·04), or in a hot solution of tartar emetic, 5—20 grams per litre, for a few minutes. For grey or black, the tannin-prepared cotton is worked for $\frac{1}{2}$—1 hour in a solution of acetate or nitrate of iron, 1°—4°Tw. (Sp. Gr. 1·005—1·02). If the tannic acid solution contains 1 centigram per litre, a perceptible grey tint is produced; with 0·5 grams per litre, and an immersion lasting one hour, one metre of calico may be dyed a moderately deep grey colour; with 20 grams per litre, a very deep grey; and with 100 grams per litre, a black.

The drying and steaming of tannin-prepared cotton *yarn*, although it would yield deeper shades, is avoided, partly on economical grounds, but also because the yarn would tend to be unevenly prepared.

The dyer of calico and mixed goods (cotton and wool) adopts, as a rule, an unimportant modification of the steeping method, using always cold or at most tepid solutions of tannin.

When plain colours are required by the calico-printer the padding method is adopted, or the thickened tannic acid solution is printed. After drying, the padded or printed calico is steamed, passed through tartar-emetic solution, and washed. It is then ready for dyeing with the requisite coal-tar colour solution.

The following method is frequently employed by the calico-printer:— The usual iron, aluminium, or other mordants are printed, aged, and fixed in the ordinary manner, and the goods are then dyed in a tannin bath with the addition of glue-size, in order to keep the unprinted parts (the "whites") unsoiled. A slight soaping at 60° C. and washing remove the tannin from the unmordanted portions. The goods are then ready for dyeing with the desired colour solutions. In this method, the ordinary mordants are changed into tannates, and the process admits of the mordants being discharged at certain points by printing over them with acid "covers," so as to produce a pattern previous to dyeing with tannin.

Similar effects can be produced by printing on the calico a thickened mixture of mordant, tannic acid, and tartaric acid, drying, steaming, and dyeing.

Still another method employed by the printer is to print on the calico a thickened mixture containing tannic acid, tartaric acid, and coal-tar colour solution; then dry, steam, and pass through tartar-emetic solution, and wash or boil with soap. The tartaric acid used in the last two cases acts as a solvent for the compound of tannic acid and metallic oxide or colouring matter, and prevents the soiling of the printing-colours by iron.

In its capacity as a fixing-agent for aluminium mordants, tannic acid, in the form of Sumach, has long been used by the Turkey-red dyer. Its mode of application is given on page 432.

187. *Application to Silk.* — Tannin matters are largely employed by the silk-dyer, partly for the purpose of adding weight to the silk, and partly as the basis of certain black dyes.

Silk is able to absorb as much as 15 per cent. of its weight from a cold solution of tannic acid without its brilliancy or feel being injuriously affected; it seems, indeed, to gain slightly in strength. From a hot solution silk will gain as much as 25 per cent. of its weight, and this more rapidly even then from a cold solution. At 70° C. the action is already nearly complete, the maximum effect being reached a little below the boiling point.

Although the tannic acid seems to be well fixed, and resists washing with water, a solution of soap, especially if warm, is able to remove the whole of the tannic acid, leaving the silk slightly tinted, and with its original properties more or less modified.

The action of tannic acid on silk is regarded by some as a chemical one; it seems, at any rate, to be similar to that which it has upon animal skins. Tanned silk does not allow endosmose and exosmose to take place throughout its substance. This is well seen by the fact that, whereas raw and boiled-off silk absorb considerable quantities of basic ferric sulphate (*see* p. 185), tanned silk has to a large extent lost this property.

When tannic acid is applied to silk for the purpose of yielding a black dye, the silk is repeatedly steeped in tepid solutions of tannic acid (chestnut extract) and pyrolignite of iron.

OIL AS A MORDANT AND AS A FIXING AGENT FOR MORDANTS.

188. **Use of Oils in Dyeing.**—The fact that fatty matters can be advantageously employed by the dyer has been recognised from very early times. The

ancient Hindoos, when intending to dye calico red by means of Madder, were in the habit of first steeping the cloth in milk and then exposing it to the sun. In later years, in the process of dyeing Turkey-red (the modern descendant of the ancient Hindoo red), the preparation of the cloth with olive or other oils forms one of the most characteristic features. The particular *rôle* of the oil in this process and the chemical changes which it undergoes have been fruitful sources of discussion, and even now different opinions on these points are held by chemists.

Of the various modern views as to the part which the oil plays, when fixed upon the fibre, the most rational seems to be that it acts largely as a *fixing-agent* for the aluminium mordant employed.

Soon after the introduction of the coal-tar colouring matters, it was noticed that oil-prepared cotton, suitable for Turkey-red, could be readily dyed with those of a basic nature. In this case the modified oil acts the part of a *mordant* in the same way as tannic acid.

189. Olive Oil, and Castor Oil.—These oils are representatives of the large class of those fatty matters which are to be considered as the glycerine salts or ethers of various fatty acids.

The essential constituent of olive oil is *trioleïn* $C_3H_5(O{\cdot}C_{18}H_{33}O)_3$, the free fatty acid of which is oleic acid, $C_{18}H_{33}O{\cdot}OH$.

Olive Oil is, however, a mixture of two fatty matters, the other constituent being *tripalmitin*, $C_3H_5(O{\cdot}C_{16}H_{31}O)_3$, *i.e.*, the glycerine compound of palmitic acid. This substance separates from olive oil in a more or less crystalline state during cold weather.

Exposed to the air for a lengthened period, olive oil becomes rancid, a change which is owing to the liberation of free fatty acid. Subjected to the action of steam, it is also partly decomposed, and again free fatty acid is produced. By boiling with caustic or carbonated alkalis, olive oil is saponified; in other words, it is decomposed, glycerine being liberated with production of an alkali compound of the fatty acid, *i.e.*, soap. When the oil is merely well shaken with a dilute solution of alkali, saponification does not take place, but there is produced a white milky liquid or *emulsion* in which the oil is suspended in an extremely fine state of subdivision. The presence of a little free fatty acid is decidedly favourable to the production of an emulsion of some permanence.

Emulsive oil (Fr., *huile tournante*) is simply olive oil more or less rancid, and hence well adapted for producing a tolerably permanent emulsion.

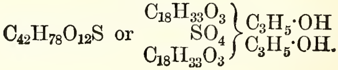
By the action of concentrated sulphuric acid upon olive oil the latter is decomposed, and very complex substances are produced, the nature of which has been explained by the researches of Liechti and Suida. Two parts by weight of olive oil are well mixed with one part of sulphuric acid 168° Tw. (Sp. Gr. 1·84), taking care to keep the mixture cool. After standing for twenty-four hours, the mixture is washed with a solution of common salt to free it from excess of acid.

The product of the reaction consists essentially of two substances distinguishable from each other by reason of their differing solubility in water and ether. Both substances are of an oily character, and possess acid properties.

The following equation possibly represents the reaction which takes place :—

$$\underset{\text{tri-oleïn.}}{2C_3H_5(C_{18}H_{33}O_2)_3} + 7H_2SO_4 = \underset{\text{oxyoleïc-glycerine, sulphuric-ether}}{C_{42}H_{78}O_{12}S} + \underset{\text{oxyoleïc-acid.}}{4C_{18}H_{34}O_3} + 6SO_2 + 4H_2O.$$

The substance which is very soluble in water and only slightly so in ether is a so-called compound-ether, bearing the name *oxyoleïc-glycerine-sulphuric-ether*, and possessing the following composition :—



$$C_{42}H_{78}O_{12}S \text{ or } \left.\begin{matrix}C_{18}H_{33}O_3\\SO_4\\C_{18}H_{33}O_3\end{matrix}\right\}\begin{matrix}C_3H_5\cdot OH\\C_3H_5\cdot OH.\end{matrix}$$

When boiled with dilute caustic alkali, it decomposes with the production of insoluble oxyoleïc acid, glycerine, and sulphuric acid. Its alkaline compound is soluble, but those of the alkaline earths and heavy metals are insoluble; they are readily obtained by mixing its aqueous or alkaline solutions with solutions of the metallic salts. The aluminium compound $[Al_4(C_{42}H_{74}O_{12}S)_3]$ is a white or slightly yellowish body.

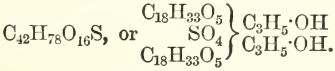
The substance which is insoluble in water but soluble in ether is *oxyoleïc acid* ($C_{18}H_{34}O_3$). It is readily soluble in alkaline water, forming a soapy liquid, which produces with solutions the salts of the alkaline earths, earths, and heavy metals, tarry or flocculent precipitates very soluble in ether.

A secondary reaction seems also to take place, probably giving rise to the production of an intermediate and unstable ether derivative of oxystearic acid. This is decomposed during the washing with water, and produces sulphuric acid, and *oxystearic-glycerine-sulphuric-ether* ($C_{42}H_{82}O_{12}S$) and *oxystearic acid* ($C_{18}H_{36}O_3$).

$$\underset{\text{Tri-oleïn.}}{2(C_{18}H_{33}O_2)_3C_3H_5} + 7H_2SO_4 + 8H_2O = \underset{\substack{\text{Oxystearic-}\\\text{glycerine-sul-}\\\text{phuric ether.}}}{C_{42}H_{82}O_{12}S} + \underset{\substack{\text{Oxystearic}\\\text{acid.}}}{4C_{18}H_{36}O_3} + 6H_2SO_4.$$

Castor oil consists essentially of the glycerine compound of ricinoleïc acid, $C_{18}H_{33}O_2\cdot OH$, and has the composition $C_3H_5(O\cdot C_{18}H_{33}O_2)_3$.

If in the above reaction castor oil be substituted for olive oil, similar substances to those just mentioned are produced, namely, *trioxyoleïc-glycerine-sulphuric-ether*;—



$$C_{42}H_{78}O_{16}S, \text{ or } \left.\begin{array}{c} C_{18}H_{33}O_5 \\ SO_4 \\ C_{18}H_{33}O_5 \end{array}\right\} \begin{array}{l} C_3H_5\cdot OH \\ C_3H_5\cdot OH. \end{array}$$

and *trioxyoleïc acid* ($C_{18}H_{34}O_5$).

The castor oil product is now a commercial article, and is sold, more or less diluted with water and neutralised with caustic soda or ammonia, under the following names, *Turkey-red oil*, *alizarin oil*, *sulphated oil*, *soluble oil*, &c.

When properly made and perfectly neutralised or rendered slightly alkaline, it dissolves in distilled water, giving a perfectly clear solution. If the water contains lime, &c., the solution is more or less milky, from the formation of the lime compound.

Some commercial "soluble oils" are merely solutions of a castor oil soda-soap. These are readily made by boiling castor oil with the requisite amount of dilute caustic alkali; saponification takes place with the greatest ease.

190. *Application to Cotton.*—As a fixing-agent for aluminium or iron mordants, the method of applying oil in its several forms to cotton is given under the head of "Application of Alizarin." (*See* pp. 428, 438, 443.)

As a mordant for the basic coal-tar colours, oil is generally applied in the form of sulphated castor oil, castor oil soap, or even ordinary oil soap.

For mordanting yarn or calico, the first, second, third, and fourth operations, given on pp. 427, 438, 442, may be employed, but frequently only the first, second, and fourth are adopted, *i.e.*, the bleached material is first impregnated with the alkaline solution of sulphated oil or soap, then immersed in a solution of aluminium salt, and finally washed previous to dyeing; if dried and steamed before dyeing, the colour is faster to washing and soaping. Since in this application the modified fatty acid is the real mordanting body, the aluminium salt must be considered as only employed for the purpose of fixing it. The fact is that the metallic compounds of these modified oils are *duplex* mordants, either the basic or acid constituent of the compound may act in the capacity of mordant, according as the colouring matter employed is of the opposite character. The metallic compounds of tannic acid are in exactly the same position.

Dyed aniline colours fixed by means of oil mordants are brighter than those fixed with tannic acid, but they are not so fast to boiling soap solutions.

The calico-printer makes considerable use of sulphated oil as a general prepare for steam-alizarin and steam-aniline colours containing tannic acid, since the presence of the oil in the fibre intensifies and brightens the majority of these colours very considerably, and makes them faster to boiling soap solution. The cloth is simply padded in a neutral or slightly ammoniacal solution, more or less dilute, and dried previous to printing.

Apart from their use as mordants, sulphated castor oil and castor oil soap are largely used in finishing for the purpose of softening heavily-starched goods, or dyed cloth or yarn, which would otherwise have an unpleasant harsh "feel." The principal objection to their use for this purpose, and one which is sometimes brought against their use as mordants, is that, after a lengthened period, the goods contract an unpleasant rancid odour.

191. *Application to Wool and Silk.*—Oil mordants have not yet found any use as such for wool and silk.

Certain preparations made by mixing olive oil and sulphuric acid have hitherto been used only for softening purposes.

ALBUMEN, CASEIN, GLUE, ETC., AS MORDANTS.

192. **Albumen** is a nitrogenous animal substance soluble in cold or tepid water. Its solutions are coagulated by the addition of mineral acids and solutions of various metallic salts, and also if heated to about 70° C., in both cases the albumen being rendered insoluble.

In chemical composition it is allied to wool and silk, and when coagulated it behaves towards colouring matters like these fibres. It is because of the above properties that albumen is of use to the textile colourist.

Egg albumen is represented in its purest form by the white of egg. This is evaporated to dryness at a low temperature, and the dry soluble product thus obtained in the form of light yellow horny flakes is an article of commerce.

If kept dry, it can be stored for a considerable time without being injuriously affected; but, if damp, putrefaction sets in, and it becomes more or less insoluble in water.

Blood albumen very closely resembles egg albumen in its composition and properties. The chief difference is that it is somewhat darker in colour. It is obtained by evaporating at a low temperature the serum of the blood of oxen, &c. The commercial product has the appearance of dark brownish-olive scales. Solutions of albumen readily putrefy, especially in warm weather; this may be retarded, or even prevented, by slight additions of borax or sodium bisulphite.

193. *Application to Cotton.*—Albumen is of great use to the calico-printer for the purpose of fixing insoluble pigments—*e.g.*, ultramarine blue, chrome green, aniline-colour lakes, &c.—or soluble pigments like the coal-tar colours. The colour in question, either in the solid state as an impalpable powder or in solution, is mixed in the cold with the albumen solution; the mixture is then printed on the calico. After dyeing, the printed cloth is steamed.

The albumen thus coagulated is fixed mechanically and more or less superficially on the fibre, and holds the insoluble pigment in the same way throughout its mass. When used in the above manner for fixing the soluble coal-tar colours, the albumen itself is, as it were, dyed.

The concentration of the albumen solution must vary according to the amount of pigment to be fixed.

For purposes of dyeing with coal-tar colours, cotton may be impregnated with albumen solution, dried, and steamed, or the albumen may be coagulated by passing the cloth through dilute mineral acid. Albumen has, however, not been largely used by the dyer in this way, partly because of its expense.

In the dyeing of wool and silk, albumen finds no use, although it is still employed to a limited extent in woollen-printing.

194. Casein, or the curd of milk, sold commercially as a yellowish granular powder under the name of *lactarine*, is prepared by precipitating skimmed milk with dilute acids. Its chemical composition is similar to that of albumen, but its properties differ considerably. It is insoluble in pure water, but soluble in alkaline solutions, *e.g.*, ammonia, borax, &c. As a solvent, borax is preferable on account of its antiseptic properties. It is used occasionally by the calico-printer as a substitute for albumen. It is not coagulated by steaming, and can only serve for colours requiring a moderate degree of fastness.

195. Glue or Gelatin is a nitrogenous substance obtained by boiling bones, skins, and other animal matters with water, and evaporating their solutions at a low temperature. Its employment by the textile colourist depends upon the fact that its solutions are precipitated by tannic acid, and that the precipitate so produced attracts many of the coal-tar colours from their solutions. In this respect it serves as a fixing-agent for the tannic acid, but as a nitrogenous albuminoid substance it may at the same time act as a mordant.

FIXING-AGENTS FOR MORDANTS.

196. One of the essential conditions of mordanting is, that the mordants should be presented to the fibres in a state of solution, and that the real mordanting body should be precipitated from the solution and upon the fibre in such a manner as to be firmly fixed upon the latter.

The various methods of effecting this have been given when treating of the application of each mordant to the different fibres. Among others will have been noticed that of employing solutions of certain salts capable of forming insoluble precipitates with the mordants. Such precipitants or *fixing-agents* deserve to be specially, even if only briefly, referred to. Those fixing-agents, which under certain circumstances act as mordants themselves (*e.g.*, fatty acids, tannic acid, gelatin, stannic chloride), have already been considered. Of the rest the following are important:—

197. Sodium Hydrate (NaHO).—A solution of this substance is used for the purpose of precipitating and fixing upon cotton ferric and manganic oxides, which in themselves serve as colours. For other mordants—*e.g.*, stannic oxide and alumina—it serves as a solvent. It is largely employed in cotton bleaching, and is of general use as an alkali for neutralising acids, &c.

198. Sodium Phosphate ($Na_2HPO_4 \cdot 12H_2O$).—This salt is used with advantage as a general precipitant for aluminium mordants. In special styles of work, *e.g.*, the production of red and pink on Turkey-red prepared cloth, it gives excellent results. It is sometimes used by the calico-printer and dyer for the same purpose, but its expense prevents it from being so extensively employed as it otherwise would be.

199. Sodium Arsenate ($Na_2HAsO_4 \cdot 12H_2O$).—This salt occurs in commerce in the dehydrated state, in sinter-like masses, generally containing common salt and about 50—55 per cent. sodium arsenate. As a fixing agent for mordants it behaves very like sodium phosphate. It is extensively used by the calico-printer as a substitute for cow-dung in the so-called operation of "dunging" or "cleansing."

The use of such a poisonous salt for this purpose is not followed by the injurious consequences one might at first sight expect, since it is either washed out of the cloth subsequently, or is fixed thereupon in an insoluble and innocuous form. To the cotton-yarn-dyer who works his material in the solution by hand, this salt is not to be recommended as a fixing-agent, since it readily causes ulcerated sores on the hands of the workmen. It must be borne in mind, too, that its employment may entail contamination of the neighbouring stream with a poisonous salt.

200. Sodium Tetrasilicate or Silicate of Soda, $Na_2Si_4O_9$.—Under the name "soluble glass," this compound is met with in commerce in the solid form. In solution, it can be used as a fixing-agent for aluminium and other mordants on cotton. It has, however, not found very general employment in England for this purpose, since there is always the risk that excess of caustic or carbonated alkali may be present, in which case alumina, more or less fixed on the fibre by drying or ageing, would be partly dissolved off again, and lead to unsatisfactory results. Well-made silicate of soda is, however, free from defects of this kind, except through the tendency of its solutions to dissociate and form a mixture of acid and basic silicate. Mordants not soluble in alkali —*e.g.*, those of iron and chromium—are not injuriously affected by sodium silicate. Aluminium mordants fixed by means of silicate of soda do not attract colouring matter so readily in the dye-bath as if fixed by sodium arsenate, nor are the colours produced so bright.

201. Sodium Carbonate ($Na_2CO_3 \cdot 10H_2O$).—This salt constitutes the "soda crystals" or "washing soda" of commerce. The salt $Na_2CO_3 \cdot H_2O$, is sold in an almost chemically pure state under the name of "crystal carbonate." It is largely used for purposes of neutralising acid liquids, and in a crude calcined form as soda-ash in bleaching cotton. It serves as the most useful fixing agent for ferric and chromic oxides on cotton; in the former case its solution is used cold; in the latter boiling hot.

202. Ammonia (NH_3).—This gas, dissolved in water, serves for general purposes of neutralising. It serves as a fixing-agent for lead acetate, but for fixing aluminium and iron mordants on cotton it is unsuitable, not only on account of its volatility, but because it does not give such good results as sodium phosphate and arsenate.

203. Ammonium Carbonate [$H(NH_4)CO_3 + NH_4CO_2NH_2$].—This commercial salt forms a white, semitransparent, fibrous mass. When it is dissolved in water, the carbamate, $NH_4CO_2NH_2$, is changed into the normal salt, $(NH_4)_2CO_3$. According to Liechti and Wolf, it is one of the best agents for fixing alumina upon cotton. Make a solution containing 40 grams of ammonium carbonate per litre, and use it cold, or at a temperature of 45°—50° C.

204. **Calcium Carbonate** ($CaCO_3$).—As ground chalk or "whitening," this substance is frequently employed for the purpose of neutralising acid liquids, and forms occasionally an excellent fixing-agent for alumina and other mordants upon cotton, *e.g.*, upon oil-prepared calico. As an addition to the alizarin dye-bath, it has long rendered essential aid to the full development of the ultimate colour, though it is now advantageously replaced, in many instances, by calcium acetate.

205. **Antimony Potassium Tartrate** [$K(SbO)C_4H_4O_6$].—This salt, better known as "tartar-emetic," is only slightly soluble in water. It precipitates a solution of tannic acid, especially if neutral salts are present, *e.g.*, $NaCl$, NH_4Cl, &c. Tartar-emetic, employed for fixing tannic acid in its capacity as a cotton mordant for basic coal-tar colours, gives most satisfactory results.

One important point to be remembered is that, with continued use, a tartar-emetic bath becomes ineffective and even injurious before it is quite exhausted. Through the abstraction of antimony there is a gradual accumulation of acid potassium tartrate in the bath, which tends to dissolve the antimony tannate or colour-lake from the fibre.

A good substitute for tartar-emetic is the cheaper antimony potassium oxalate [$K_3Sb(C_2O_4)_3 \cdot 6H_2O$]. It is more sensitive and gives up its antimony more readily than the tartrate, hence the bath becomes sooner charged with acid-potassium-oxalate; the duration of the fixing process should therefore not be prolonged beyond, say, one minute, and the solution should be weak.

Antimony hydrate freshly precipitated from antimony chloride by means of sodium carbonate, then washed and suspended in water, is even more economical as a fixing agent for tannic acid, and is said to possess the further advantage of not leaving the bath acid.

206. Potassium Ferrocyanide [$K_4(Fe{\cdot}Cy)_6{\cdot}3H_2O$].—This salt and also *potassium ferricyanide* $K_3(FeCy)_6$ have long been used by the dyer and calico-printer in conjunction with iron salts for the production of Prussian Blue. With solutions of several of the basic coal-tar colours they produce precipitates, and hence may, in certain cases, be employed as mordants for cotton in place of tannic acid.

ASSISTANTS.

Under this head may be included all those substances of use to the dyer which cannot be classed as colouring matters, mordants, or fixing-agents. It is, however, only intended to enumerate here a few of those which are more prominent, and to refer briefly to some of their applications.

207. Tartaric Acid [$C_4H_4O_4(OH)_2$].—This substance is sold in the form of hard, colourless crystals, readily soluble in water. It is used by the calico-printer in the production of steam-blue, steam-green, aniline-black, &c.; also as a resist for aluminium and other mordants, and in the discharge colours for Turkey-red. It is occasionally used by the woollen dyer as an addition to the mordanting bath, *e.g.*, in conjunction with potassium dichromate, alum, stannous chloride, &c. The silk-dyer employs it as an agent for brightening colours after dyeing. In some cases tartaric acid may be advantageously replaced by *oxalic acid.*

208. Acid Potassium Tartrate [$C_4H_4O_4(OH)(OK)$].—This salt is better known as *cream of tartar* or *tartar.* It forms hard, colourless crystals, but is more usually sold as a white crystalline powder. In its crude state it is called red or white "argol," according as it has been deposited during the fermentation of red or white wine.

It is extensively employed by the woollen-dyer as an addition to the mordanting bath, *e.g.*, in conjunction with alum, stannous chloride, &c. In such cases, double decomposition undoubtedly takes place, and the corresponding tartrates, or double salts, which are formed, seem to be more suitable as mordants than the original salts. Why this is so has not yet been determined, but probably the alumina is fixed upon the fibre in larger amount and in a more suitable form; no doubt, too, if the liberated tartaric acid absorbed by the fibre is improperly washed out, it will be less injurious in the dye-bath than the sulphuric acid of the alum would be. Certain it is that the addition of tartar to the mordanting bath, in suitable amount, adds fulness and brilliancy to the ultimate colour. By mordanting wool with pure tartrates of aluminium, &c., excellent results are obtained.

Owing to the comparatively high price of cream of tartar many substitutes for it have been proposed, and also employed.

These bear such names as "tartar substitute," "pro-argol," &c., and generally consist of mixtures containing oxalic acid, bisulphate of potash, alum, common salt, &c. "Essence of tartar" is a solution of tartaric acid, frequently adulterated with sulphuric acid.

"Super-argol" is said to be a mixture of white argol and sulphuric acid, the latter present in amount sufficient to combine with the potash.

It may be confidently asserted that all these substitutes, if at all useful, can be made more cheaply by the dyer himself, and, as a general rule, the real value and economy of all articles bearing fancy names may be doubted. In those cases where the use of tartar or argol depends entirely or mainly upon their acid properties, cheaper acid salts may frequently replace them with advantage, but not where their action is due to the property they possess of forming double salts.

209. Acetic Acid [$C_2H_3O(OH)$]. — This acid, also known in its dilute and less pure form as "vinegar," is largely obtained as a product of the dry distillation of wood, and by the oxidation of dilute alcoholic liquids. It is of very general use—*e.g.*, as a solvent for colouring matter—to acidify dye-bath solutions, to neutralise calcareous water, as an addition to printing colours, &c.

210. Acetate of Lime [$Ca(C_2H_3O_2)_2 \cdot 2H_2O$].—This salt is prepared by dissolving chalk or calcium carbonate in acetic acid. It is used as a solution, and should be as free from iron as possible. The best commercial product sold as a white powder contains about 90 per cent. $Ca(C_2H_3O_2)_2$. In a more or less crude form, namely, as pyrolignite of lime, it is largely employed for the purpose of making commercial aluminium acetate (red liquor).

It is of very special value as an addition to the dye-bath when using non-calcareous waters in dyeing with several colouring matters, *e.g.*, Alizarin, Logwood, Brazilwood, Weld, &c.

The exact *rôle* of the lime-salt in such cases is, perhaps, not yet fully determined. The view which seems to explain known facts the best is that the calcium forms a necessary constituent of the coloured lake fixed on the fibre. In woollen dyeing, it will certainly have the primary effect of neutralising the acidity of the mordanted fibre.

211. Sulphuric Acid (H_2SO_4).—This acid is extensively employed as an assistant in the dye-bath by the wool- and silk-dyer when applying those "acid colours," which consist of the alkali salts of sulphonic acids, *e.g.*, Azo-scarlets, Indigo Carmine, &c. It is also frequently employed along with potassium dichromate in the mordanting of wool (*see* p. 209). It serves generally for neutralising alkaline solutions.

212. Sodium Sulphate ($Na_2SO_4 \cdot 10H_2O$).—This salt, also known as *Glauber's salt*, is extensively employed by the woollen-dyer as an aid to obtain even, regular, or level dyeing.

Being very soluble, it raises the Specific Gravity and the boiling point of the dye-solution if used in large amount, and this fact alone may possibly be of some little service in certain dyeing operations. The shade of an aniline violet, for example, can be made reddish or bluish, according to the temperature of the dye-bath.

When added to a woollen dye-bath as a "levelling-agent," it tends to render the colouring matter less soluble, and the latter is then only attracted gradually by the wool, as it dissolves.

Sometimes it may be necessary or convenient, in dyeing compound shades, to add to an acid dye-bath colouring matters whose dyeing power is actually diminished by the presence of acid, *e.g.*, Orchil, Magenta, redwoods, &c. In such a case, the addition of sodium sulphate to the dye-bath causes them to dye better, since it tends to reduce the acidity of the bath by combining with the free sulphuric acid used to form sodium bisulphate. If the addition of the sodium sulphate is regulated, it is even possible to determine the rapidity with which the wool shall take up such colouring matters, and a means of shading is thus afforded. In order to prevent excessive felting of woollen yarn it may sometimes be preferable indeed to shade in this manner, rather than to remove the textile material frequently from the dye-bath, for the purpose of adding fresh colouring matter. If, by mistake, an excess of colouring matter should be added, a further addition of sulphuric acid will rectify the error. A similar example is afforded in the dyeing of red, brown, and grey shades on wool mordanted with potassium dichromate, where Logwood or Peachwood are used in small amount. To prevent these dyewoods from giving up their colouring matter too rapidly, and thus dyeing unevenly, one may either add a large amount of sodium sulphate from the beginning, or first a little sulphuric acid, and afterwards sodium sulphate gradually. By the first plan, the colouring matter is made to dissolve gradually; by the second, its dyeing power is diminished, and only developed on the addition of the sodium sulphate.

The prevention of too rapid and consequently uneven dyeing by the use of sodium sulphate is exemplified in dyeing with Indigo Carmine, Azo-scarlet, and other acid colours.

213. **Boiled-off Liquor.**—This is the soapy liquid which has been employed for the purpose of removing the silk-glue from raw-silk previous to dyeing. It is, hence, a slightly alkaline, more or less concentrated, solution of silk-glue. To the silk-dyer it serves much the same purpose as sodium sulphate does to the woollen-dyer, especially in the application of coal-tar colours. If added to the dye-bath in suitable amount, it causes the colouring matter to be attracted more slowly and evenly by the silk. It also preserves the lustre of the latter. If used in excess, it is very injurious, since it wastes colouring matter and destroys the lustre of the silk. As a suitable amount for most cases, 50—100 cubic centimetres of boiled-off liquor per litre of dye-bath solution may be employed.

When this liquor is not obtainable, it can be replaced, with more or less success, by a solution of soap and gelatin.

METHODS AND MACHINERY USED IN DYEING.

CHAPTER XII.

NOTES ON COTTON, WOOL, AND SILK DYEING.

214. Methods of Cotton Dyeing.—Owing to the slight attraction which cellulose has for the great majority of colouring matters, the method of dyeing cotton usually comprises the two operations of mordanting and dyeing.

As a general rule, these operations are perfectly distinct, and follow each other in the order given. This is decidedly the most rational plan; it yields the best results, both with respect to brilliancy and depth of colour, and to fastness against washing, soaping, &c.

In some cases the " one-dip " method—*i.e.*, dyeing in a single bath containing both colouring matter and mordant —is adopted, *e.g.*, for logwood and copper sulphate blacks. This plan, however, is by no means of general application, and although saving time and labour, it never gives such good results as can be obtained by the first method. Of course where no mordant is required—*e.g.*, in indigo-vat-blues, aniline black, &c.—a single bath only is necessary.

Another plan, frequently adopted, but by no means the most rational, is first to impregnate the cotton with a solution of colouring matter, and then in a separate bath to apply the mordant, as in certain logwood blacks. It invariably gives pale colours, because the absorbent power of cotton is too limited to take up the necessary amount of colouring matter; hence the operations require to be repeated several times, or very concentrated colour solutions must be used, to obtain a satisfactory result. The principle of the process really consists in precipitating on the fibre successive layers of pigment (compound of colouring matter and mordant), and, indeed, in a most superficial manner, so that the dyes obtained by this method are never so fast to rubbing or washing as those produced by the first method alluded to.

Sometimes, for example, in the production of catechu browns, the last-mentioned method is the best possible; but in this case the cotton has a marked attraction for the active principle of the Catechu applied in the first bath, and absorbs large quantities of it. The potassium dichromate used in the second bath serves rather as an oxidising agent than as a mordant.

215. Operations, &c., in Cotton Dyeing.—Cotton is dyed in all stages of manufacture, namely, as loose cotton-wool, cotton yarn or thread, either in hank or "chain" (warps), and as cotton cloth (calico).

It is mostly dyed in the form of yarn or cloth, but in recent years raw-cotton has been extensively dyed for the purpose of mixing with dyed wool previous to the "scribbling" process. Only in few cases can really satisfactory colours be obtained, able to withstand the subsequent scouring and milling processes of the woollen manufacturer (*e.g.*, aniline blacks, catechu browns, &c.).

When light shades of colour are to be dyed, the cotton, in whatever state it may be, should be thoroughly bleached. For dark colours (in order to ensure even dyeing afterwards) it suffices to boil the cotton well with water, preferably with the addition of sodium carbonate.

Raw-cotton is apt to become matted by such preliminary boiling, and the operation is usually omitted; but it is invariably done with cotton yarn. As to calico, all sizing material, at least, should be removed, even if further bleaching be not attempted.

There is a prevalent opinion that cotton should only be dyed in the cold, but it is altogether a mistaken one. When, for example, it is possible to fix the necessary mordant on the fibre in a thoroughly insoluble state, cold dyeing is not to be recommended, except where a high temperature would destroy the brilliancy of the colour. Cold or tepid dyeing is employed when the mordant applied is more or less soluble; for example, if tannic acid only is used, or if the colour-lake is soluble in hot water, *e.g.*, ordinary azo-scarlets on cotton. In some cases the employment of a high temperature is absolutely necessary, as, for instance, when the colouring matter used is not very soluble, *e.g.*, Alizarin.

The various devices for ensuring "level" dyeing will be treated of in "Notes on Wool-Dyeing" (*see* p. 276.)

216. Unspun Cotton Wool.—*Dyeing Machinery.*—The dye-vessel employed for raw-cotton is similar to that described as being used for loose-wool (*see* p. 277). Direct fire heat is seldom or never adopted. In recent years various novel arrangements have been proposed and patented, but their practicability has yet to be proved, *e.g.*, vacuum-dyeing machines.

Washing Machinery.—The washing of raw cotton may be effected by the raw-wool scouring machine (*see* p. 100).

Excess of water is removed by passing it between a pair of squeezing rollers, or by means of the centrifugal machine (hydro-extractor).

Drying Machinery.—Raw cotton may be dried on the machines described as being used for loose-wool (*see* p. 277).

217. Cotton Yarn.—*Dyeing Machinery.*—For hank-dyeing the simplest method is to work the hanks in the dye liquor by hand in the manner described for woollen yarn scouring on p. 105.

With large quantities of any single colour, *e.g.*, Turkey-red, logwood-black, indigo-blue, &c., the employment of dyeing machines becomes almost imperative.

Figs. 48 and 49 represent an excellent machine, designed by A. Wilson, of Paisley.

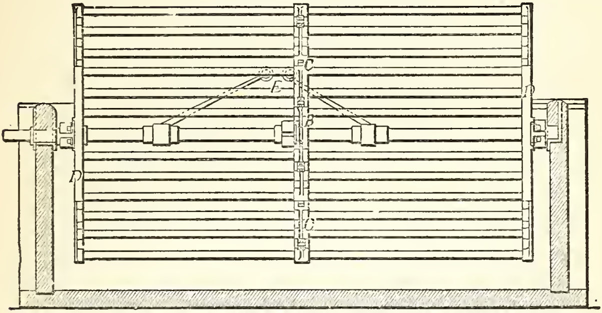


Fig. 48.—Hank-Dyeing Machine.

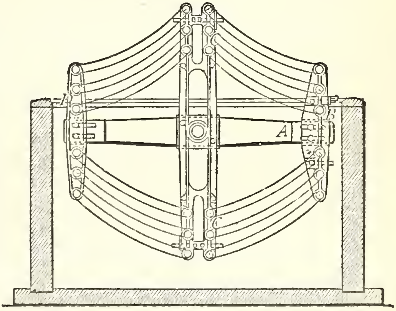


Fig. 49.—Section of Fig. 48.

It consists of an ordinary rectangular wooden dye-vat fitted with a four-armed skeleton-winch, upon which the rods, previously filled with yarn, can be readily suspended. In charging the machine, the arm A is brought into the upright position, the movable portion B is lifted off the cross piece, and the hinged portion at C is turned back. The hanks of yarn are hung on pairs of light wooden rods; these are placed in the sockets at B and C, and then securely fastened down by replacing the movable portions alluded to. The winch is then turned round, and the other half is filled with hanks in a similar manner; B represents the arrangement of sockets with movable caps in the central part of the winch, D that at the ends where there are no movable parts, the ends of the rods being merely pushed into the sockets. When the dyeing is finished, the whole winch full of yarn can be raised with a travelling crane out of the dye-vat by the rings E, and lowered into another vat for washing, &c.

Another hank-dyeing machine, that of E. Boden, is represented in Fig. 50, the back portion only being exhibited.

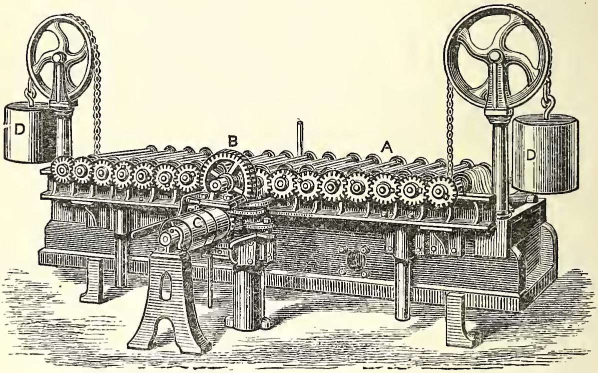


Fig. 50.—Boden's Hank-Dyeing Machine.

It consists of a wooden dyebeck, provided with a light iron frame carrying a series of reels A geared with each other at one end. The frame, together with reels, is counterbalanced by means of large weights D, and can be readily raised or lowered by a hydraulic ram in the centre. When raised, the front ends of the reels are free to be filled with yarn; when lowered, the hanks are immersed in the dye liquor. By means of the pulleys at C, the large cog-wheel B is made to revolve in alternate directions, and the motion is transmitted to the cog-wheel of the reel immediately behind. This alternating motion is necessary in order to keep the yarn well opened out, and to prevent it from becoming entangled.

When the cotton yarn is in the chain form, being intended for warps, a machine similar to that represented in Fig. 51 is employed. In its simplest form—namely, as a single-box machine—it consists of a rectangular wooden dyebeck A, fitted above and below with a series of wooden rollers, and at the end with a pair of squeezing rollers. The machine represented is a two-box machine, and is simply a duplication of that just described. Six or eight warp-chains G, separated by the guide-pegs at H, are passed side by side through the two boxes A and B in the direction indicated. The squeezing rollers C D prevent as much as possible the liquor in A from being drawn over by the warps into B, which contains a different liquid. As the warps pass out of the machine, the squeezing rollers E F remove excess of liquid to facilitate the subsequent drying. At J the warps are again separated by guide pegs, and withdrawn from the machine by the reel K. The steam pipes L L serve for heating the solutions employed. Some machines (*e.g.*, those used for dyeing logwood-blacks) have as many as six boxes, each box being filled with a different liquid, which may serve for mordanting, dyeing, washing, &c. The whole machine is specially arranged to make the several operations continuous.

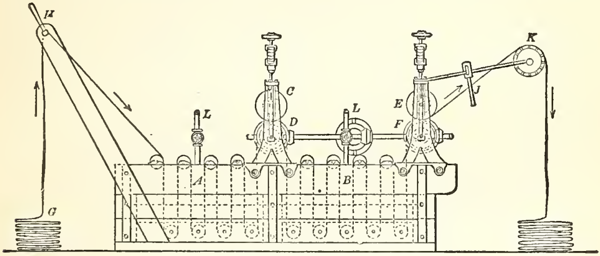


Fig. 51.—Warp-Dyeing Machine.

Washing Machinery.—A very old form of washing machine is the so-called "wash-stocks," represented in Fig 52. It consists of a stout wooden or iron box A of special shape, in which are placed the bundles of yarn F to be washed. Two heavy wooden hammers B and C, suspended loosely at D, are alternately raised by the cams on the revolving shaft E, and fall on the yarn in such a manner that its position is continually changed. A perforated pipe H supplies the trough with a copious supply of water.

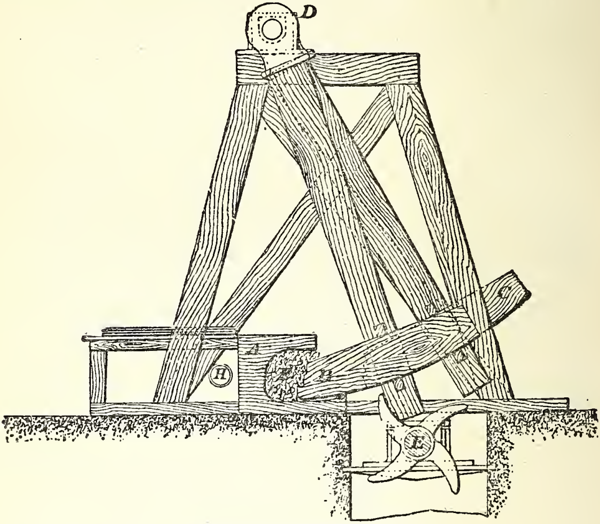


Fig. 52.—Wash-stocks.

One of the best forms of modern hank-washing machines is that shown in Figs. 53 and 54, and made by Messrs. Duncan Stewart and Co., Glasgow. It consists of a U-shaped wooden trough E, with a series of radial, horizontal arms, C D, holding the yarn, supported immediately over it. The axes of the radial arms are fixed, at equal distances, to the endless chain A,

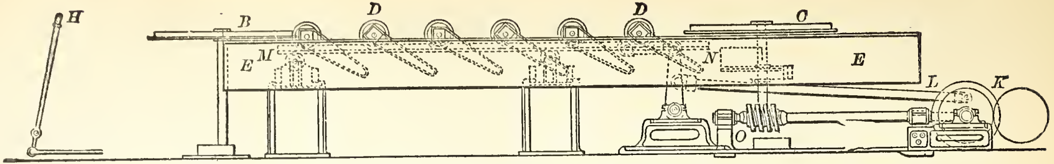


Fig. 53.—Scotch Hank-Washing Machine.

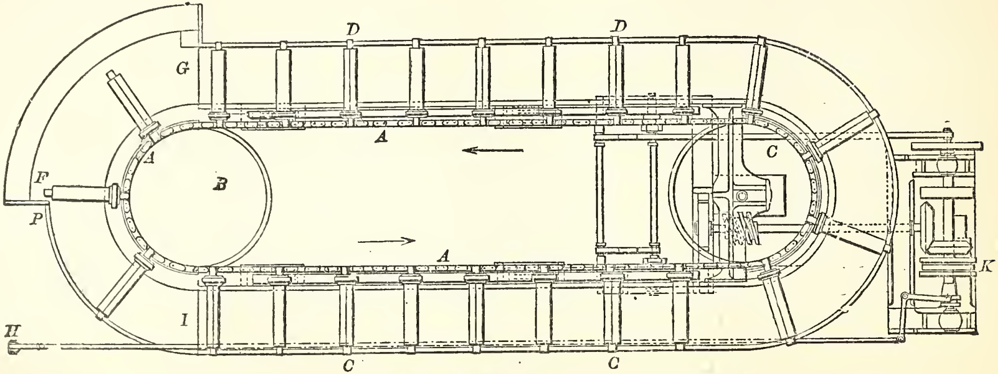


Fig. 54.—Plan of Fig. 53.

which passes round the large pulleys B and C. The square reel of each arm revolves loosely on its central axis, the end of which rests on the outer edge of the trough. At the end nearest the chain each reel has a fixed wheel or pulley. The rails M N, on which these pulleys rest, receive a vigorous to-and-fro movement transmitted by the crank shaft L, and thus cause the reels to revolve rapidly to right and left alternately, and the hanks to vary their point of suspension. By the revolution of the large pulleys B and C, actuated by the endless screw O, the radial arms receive a rapid and continuous progressive movement in the direction indicated by the arrows. At the points G and I the trough is discontinued; fresh water enters at G, and the dirty water passes out at I. As the arms pass between the space G and F, the washed hanks are removed and at once replaced by others ready for washing. These enter the trough at I, and pass round, in a direction contrary to that of the water-current, to the point G. The free, unsupported ends of the arms droop considerably between the points G and F, and they are again raised to the horizontal position by moving on to the sloping guide rail situated between P and I. The first movement is communicated through the pulley at K. The handle H is for starting and stopping the machine. The machine is made of such a size that the hanks are sufficiently washed after having made one circulation of the trough, the whole operation being really continuous.

Another excellent hank-washing machine is that of A. Weser, Elberfeld, represented in Fig. 55.

This machine consists of a cistern A, with water inlet at B, and outlet at C. Situated immediately above is a series of movable brass reels D, attached to a broad endless belt or chain E. This is caused to revolve continuously in one direction round the two large vertical pulleys F, by means of the driving pulley G, the endless band H, and the cog-wheels I.

The hanks of yarn are suspended on the reels at J, and carried along by the lower reels so as to be partly immersed in the water of the cistern A. At K they are removed, being thoroughly washed, and the empty reels above travel back to the end J. During their onward passage the hanks of yarn continuously receive vigorous and sudden backward and forward movements, since the whole system comprising the two large pulleys F, the endless belt E, and the reels D, resting on rockers L, or otherwise supported, is driven to-and-fro by means of the fly-wheel M and crank shaft N. Since, too, the inner discs of the reels rest on guide rails at O and P, each backward and forward movement of the belt and reels causes the latter to revolve rapidly on their axes alternately to right and left. The total effect of the simultaneous, onward, revolving, and to-and-fro movements described is

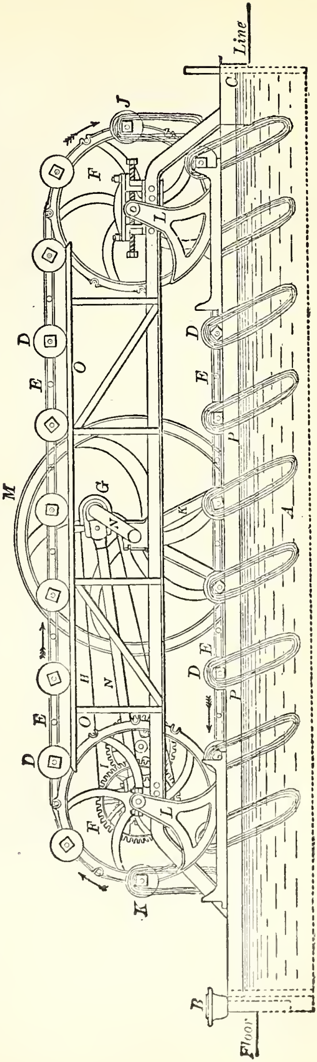


Fig. 55.—German Hank-Washing Machine.

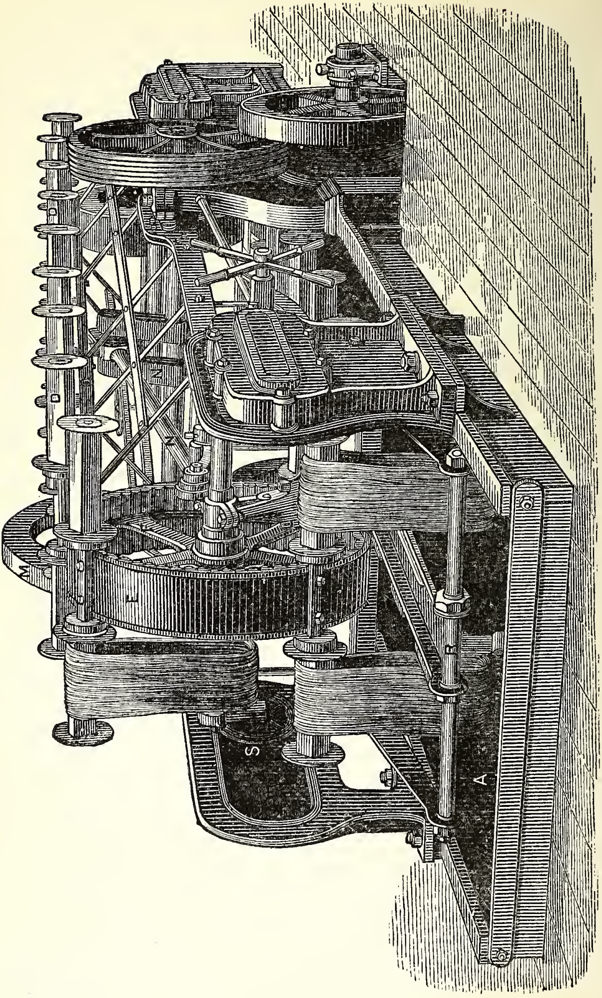


Fig. 56.—Perspective View of Fig. 55.

that the yarn is rapidly and effectually washed in a continuous manner.

Figure 56 gives a perspective view of this machine, slightly modified, in which the central system of reels, large pulleys, &c., is supported by means of the framework R, and moves to and fro on the wheels at S, instead of on rockers.

In both machines the whole action imitates in a striking manner the washing of a hank as it would be done by hand.

Excess of water is best removed from wet yarn either by means of the hydro-extractor (*see* Fig. 72, p. 281), or by the hydraulic press represented in Fig. 90, p. 435.

Drying Machinery.—Cotton yarn is dried by suspending the hanks on rods or poles, and

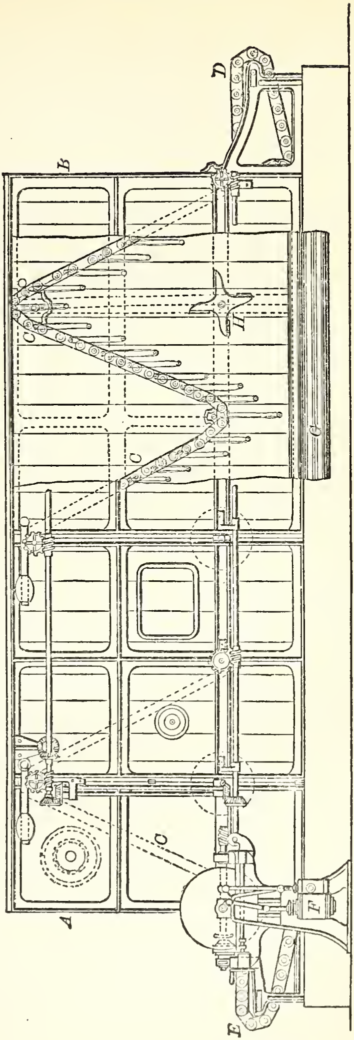


Fig. 57.—Continuous Hank-Drying Machine.

hanging these in large and well-ventilated chambers or stoves heated by means of steam-pipes.

Fig. 57 shows a continuous hank-drying arrangement of MM. Tulpin frères, Rouen. It consists of a closed wooden or iron chamber A B, provided with openings at each end for the entrance and exit of the yarn. The interior is heated by means of steam pipes, G, and contains ventilating fans H, for agitating the heated air. A ventilator situated above draws the moist air away, and causes fresh air to enter the chamber.

An endless chain C traverses the interior of the chamber in a zigzag path, and supports the ends of the rods holding the hanks of yarn. The wet yarn is introduced at one end of the chamber E, and it is taken off dry at the other D.

A small engine F supplies the power to move the endless chain.

218. Cotton Cloth.—*Dyeing Machinery.* Cotton cloth or calico is dyed in a wooden or cast-iron dyebeck, over which a winch is supported (*see* Fig. 74). The beck is divided longitudinally by a perforated diaphragm, which is open below, in order to allow the pieces to pass freely beneath it. The pieces, stitched separately in the form of endless ropes or bands, are drawn by the winch continuously in the same direction, and are prevented from becoming entangled with each other by means of a series of wooden guide pegs which divide the several pieces.

Fig. 58 gives a section of Mather and Platt's spiral dyeing machine, largely used by calico-printers.

A is the cast-iron dyebeck; B the drain beneath; C the winch; D, a perforated steam-pipe passing through the beck; E, the mid-feather or diaphragm; F, the peg-rail for keeping the pieces from entangling; G G, handles and tappet shafts for putting in motion or stopping the winch; H is the steam-valve.

About thirty to forty pieces stitched end to end are introduced at one end of the beck, and caused to pass over the winch and through the liquor in a spiral manner until the other end of the beck is reached. The first end of the cloth having been brought over the winch to the front, is passed under a small pulley and led horizontally behind the strands of cloth, under a second pulley situated at the entering end of the beck, there to be stitched to the last end of the pieces and led over the winch again. By this arrangement a long continuous band of cloth is formed which gradually traverses the whole beck in spiral fashion, yet not in a state of tension, since a few yards of slack cloth are left in the loop of each spiral. This method is adopted in order to obtain as much as possible a uniformity of dye.

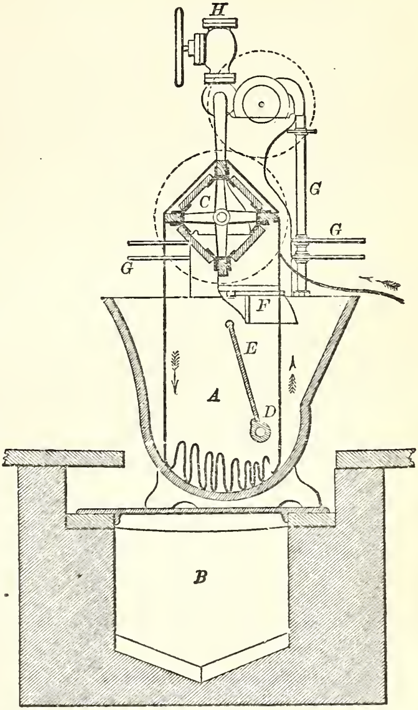


Fig. 58.—Spiral Dyeing Machine.

Quite a different dyeing machine, largely used by those who dye cotton linings, unions, &c., is the so-called "jigger," a section of which is represented in Fig. 59. In this machine the pieces are dyed in the open width. It consists of a wooden dyebeck, above which are two fixed rollers with oblique arms attached to their supports, so that a loose roller may revolve against them. The pieces to be dyed (say, five pieces of seventy-five yards each) are stitched end to end in the open width and beamed on a loose roller. This is placed on one of the oblique arms, and the piece is led down into the dye liquor beneath a wooden roller at the bottom, and then passed upward and around the fixed roller on the opposite side of the machine. When the whole length of cloth has run through the dye liquor, the movement is reversed, and the pieces are now caused to pass back through the dye liquor and on to the opposite fixed roller. In this manner the pieces are passed to and fro several times, and only during the last passage, *i.e.*, when they are properly dyed, are they again wrapped on one or other of the loose rollers. In the most complete arrangement by L. Glover, the reversing of the motion takes place automatically.

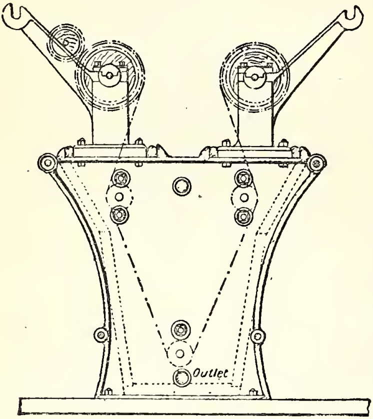


Fig. 59.—Lancashire Jigger Dyeing Machine.

Washing Machinery.—There are numerous kinds of washing machines for calico. Perhaps the oldest form of machine still met with is the "dash wheel." It consists of a large, hollow, wooden drum, divided internally into four compartments, each of which is provided with a hole for introducing the material. Jets of water are admitted by slits, and there are numerous holes in the periphery for the exit of dirty water. One or two pieces of cloth are put into each compartment of the drum, and during the revolution of the latter they are tossed from side to side.

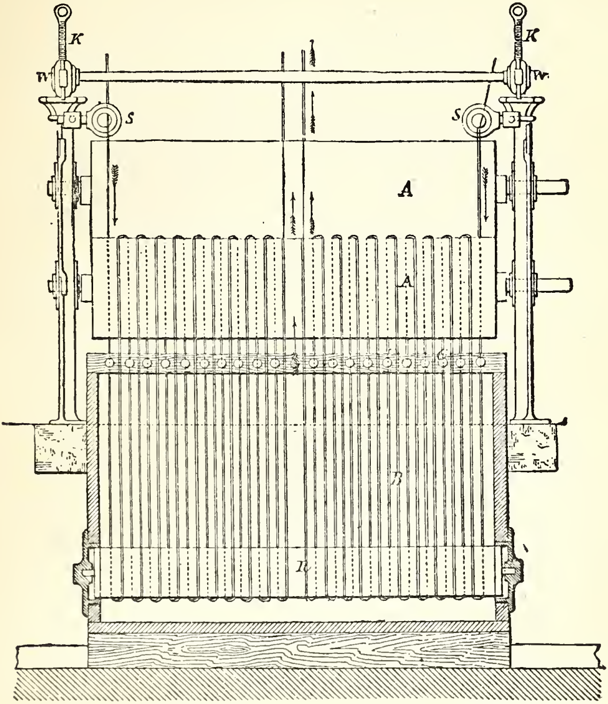


Fig. 60.—Washing Machine for Calico.

Figs. 60 and 61 represent a washing machine largely used by bleachers. It consists of a water trough, B, above which a pair of heavy wooden squeezing rollers A A, are supported. The pieces to be washed, stitched end to end in the chain form, are passed spirally between the squeezing rollers and down beneath a roller R, fixed in the lower part of the washing trough; C are guide-pegs to keep the several strands separated; G is the water-main; E the water-tap; K and W are the screws, levers, and weights for regulating the pressure of the squeezing bowls against each other; S S are strong brass rings, or "straining eyes," capable of being turned more or less obliquely, to give the proper degree of tension to the pieces on entering the machine. The diagram represents two sets of pieces being washed simultaneously, entering the machine at the ends and making their exit at the centre.

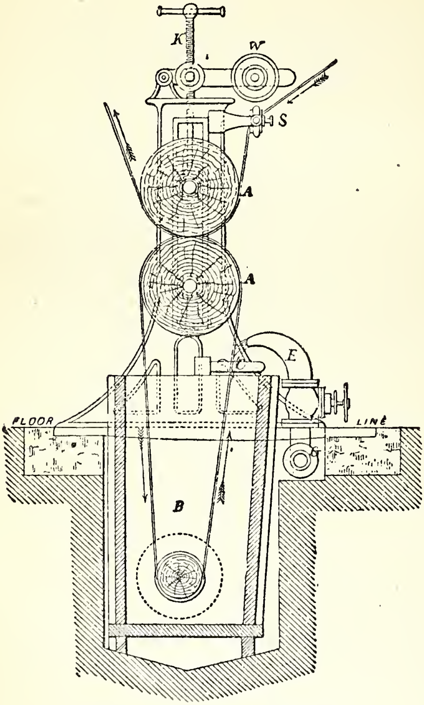


Fig. 61.—Side View of Fig. 60.

Fig. 62 represents another washing machine in which the pieces also travel spirally between a pair of squeezing rollers. The water trough in this case is shallow and provided with two rollers—a square one A, immediately below the squeezing rollers, and a round one B, with ribs. The

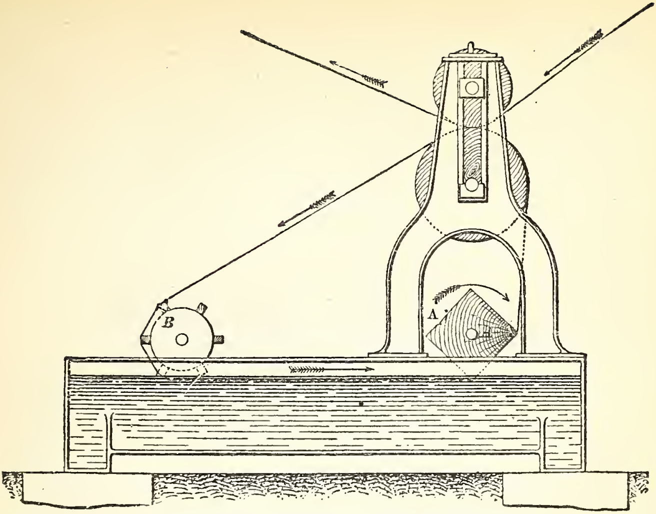


Fig. 62.—Square beater Washing Machine.

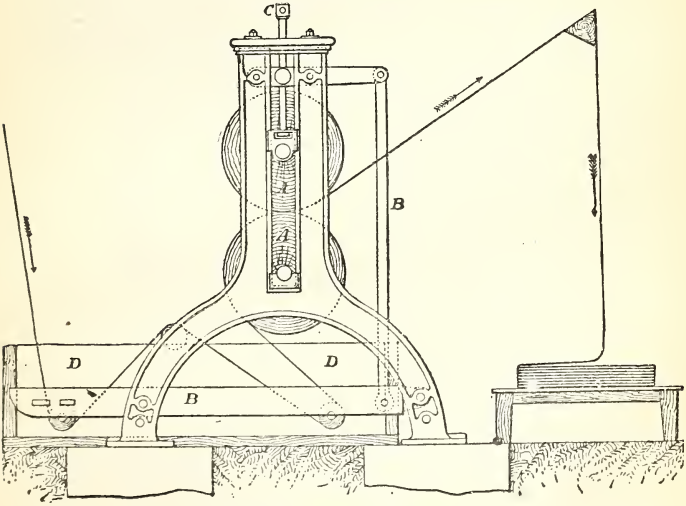


Fig. 63.—Squeezing Rollers.

square roller, or "beater," revolves in a direction contrary to that of the pieces, which thus receive a violent flapping motion while moving in a state of tension along the surface of the water. This machine serves admirably for the expulsion of particles of dyewoods, &c., from dyed pieces.

Excess of water may be removed from wet calico by means of the ordinary squeezer represented in Fig. 63. This machine consists of a pair of hard wooden rollers, A A; compound levers B B, with weights and screw C, serve to regulate the pressure of the bowls against each other. A small water trough D D is frequently situated beneath the bowls.

A more durable "squeezer" is that of W. Birch, represented in Figs. 64 and 65, and now very generally adopted in calico bleach works, &c. In this machine the cloth strand is confined and compressed in a narrow groove. The fabric E is drawn into the squeezer with tolerably uniform tension ensured by reason of the swing bar D. The tension bars T T are fixed in such a position that the cloth in going over the roller R and through the pot eye P, is somewhat tightly drawn to the bottom of the grooved roller A before it passes through the "nip;" this tension is necessary to prevent the piece from becoming damaged.

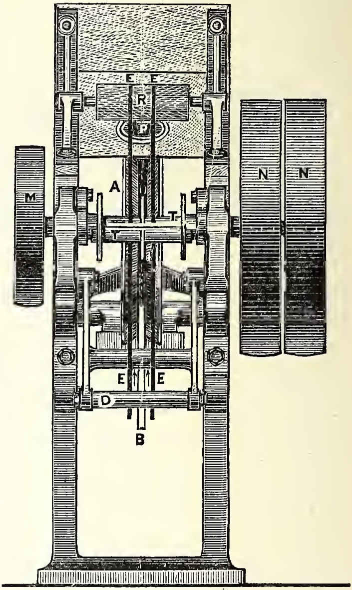


Fig. 64.—Birch's Squeezing Roller (Front view).

The cloth is drawn from the machine by means of a roller or winch actuated by the pulley M. The pressure of the brass disc B against the grooved roller A is regulated by the screw C connected with lever and spring; N N are fast and loose driving pulleys.

Drying Machinery.—Calico is frequently dried in stoves heated with hot flues or steam pipes situated in the basement (*see* p. 441).

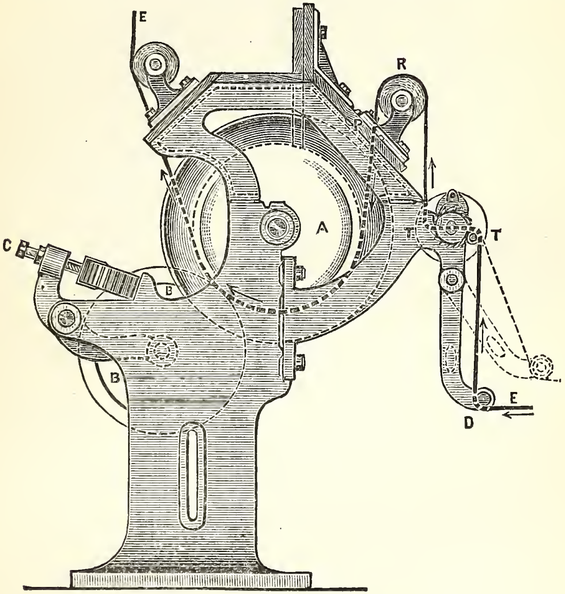


Fig. 65.—Side View of Fig. 64.

The internal arrangement for suspending the pieces varies. In some the building is one-storeyed, and the pieces are suspended in zigzag fashion from wooden rails placed near the roof, so that the loose folds come within a few feet of the iron grating over the flues. In others, the stove is divided into several storeys, each with floors of iron grating, and furnished with wooden framework having long parallel rows of upright wooden pegs. One selvedge of the pieces is passed alternately from right to left, and twisted over the pegs. By this plan of hanging it is possible to pack a much larger quantity of cloth into a given space.

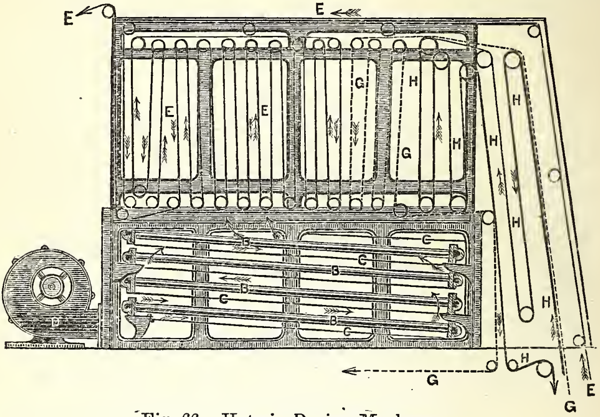


Fig. 66.—Hot-air Drying Machine.

Calico is also dried by means of the steam-cylinder drying machine described on p. 286.

When it is not desirable that the cloth should come into actual contact with a heated metallic surface—*e.g.*, in drying cloth after impregnating it with mordants which are injuriously affected by a high temperature—the pieces may be made to traverse a closed hot-air chamber fitted with wooden rollers at the top and bottom. Fig. 66 shows the arrangement used by the calico-printer for drying the pieces immediately after printing. The fan D drives a current of air in a zigzag course along the channels C surrounding the steam pipes B. The heated air passes into the upper drying chamber, there moves in a direction contrary to that of the pieces, and makes exit at the top. In this particular case three different pieces of cloth are dried simultaneously: the printed piece E, the back-cloth or grey G, and the endless blanket H.

In some cases calico is dried on the so-called "tentering" machine, similar to those used for woollen cloth (*see* p. 287).

NOTES ON WOOL DYEING.

219. Methods of Wool Dyeing.—The methods of dyeing wool differ considerably from those employed for cotton and other vegetable fibres.

Wool has a much greater affinity than cotton for most of those colouring matters in which the colour is ready formed and does not require developing by the use of mordants. Such is the case, for example, with a number of the coal-tar colours. It is sufficient in many cases to add the solution of the colouring matters to the cold or tepid water contained in the dye-bath, and after introducing the woollen material, to raise the temperature of the solution. With such colouring matters as require a mordant to develop the colour they yield, *e.g.*, Logwood, Camwood, Cochineal, &c., the exact mode of dyeing varies according to the nature of the colouring principle and the mordant. The following three methods are employed in practice:—

1. The wool is first boiled in a solution of the metallic salt or mordant, and afterwards in a fresh bath containing the solution of the colouring matter or dyewood decoction. In other words, the wool is mordanted first and dyed afterwards. Dyers sometimes call the colours dyed by this method "prepared colours." The mordanted cloth is said to be "prepared."

2. The wool is boiled in a solution of the colouring matter or dyewood decoction, and when, after some time, it has absorbed as much of the colouring principle as possible, the colour is developed and fixed on the wool by adding the mordant to the same bath. This method has been generally adopted with certain mordants which

produce dark or sombre shades of colour, and is called the "stuffing" and "saddening" method; the "stuffing" being the boiling of the wool with the dye-stuff, and the "saddening" the subsequent operation of developing the colour by adding the mordant.

3. The wool is boiled in a solution containing both colouring matter and mordant from the beginning of the operation. In this case the colouring matter and mordant combine with each other to form a coloured body which an excess of the mordant dissolves; from the solution it is gradually absorbed by the wool.

4. Combination of 1 and 2. Mordant, dye, sadden.

220. The Mordanting and Dyeing Method.—The best example of the first method is afforded in the black dyeing of wool by means of potassium dichromate and Logwood. The method can be employed with most of the natural colouring matters or dyewoods in conjunction with the following mordants—alum, potassium dichromate, chrome-alum, stannous chloride. When it is carried out in its entirety, the fabric should be well washed between the mordanting and dyeing processes, in order to prevent any mordant which is not fixed on the wool from being carried over into the dye-bath; otherwise it would not only cause loss of colouring matter by precipitating it in the bath, but might also prevent the dye-stuff from yielding its colouring matter to the solution.

One advantage of this method is, that the solutions used for mordanting and dyeing can be preserved for successive lots of material, and need only to be replenished occasionally. This implies that the mordant and colouring matter are better utilised.

Another advantage is that the dyer can "match-off" to any exact shade with very little trouble, since the mordant determines the tone of colour, and this being once fixed on the wool, the proportions of the various dyewoods required can be frequently altered until the desired shade is obtained. To ensure success in this matter it is only necessary to add in the beginning a slight deficiency of each dyewood, since it is evident that no modification of the proportions would rectify the error caused by employing an excess of dyewood. As a rule, it may be said that from a given weight of dyewood and mordant, this method of dyeing produces colours which are deeper and richer in tone, and faster against milling than those obtained by any other method.

Its only disadvantage is that it requires more time and labour, and, consequently, expense.

221. The Stuffing and Saddening Method.—The dyeing of a claret-brown by means of Camwood and ferrous sulphate is a good example of this method which is applicable with some of the natural matters. The mordants generally employed are ferrous sulphate, copper sulphate, or potassium dichromate, and occasionally alum.

When Catechu is used as the dye-stuff, the saddening is preferably effected in a *separate* bath—*e.g.*, by means of potassium dichromate—since in this case both baths can be preserved and used continuously for successive lots of woollen material.

The same may be said of dyeing the claret-brown just mentioned; indeed, the use of two baths in this method might be adopted, whatever be the colouring matter or mordant employed, but this would in many cases possess no material advantage over the method of mordanting first and dyeing afterwards.

The following are the advantages when the stuffing and saddening take place in one bath :—

The time, labour, and expense are less.

The desired tone of colour required may be sometimes obtained more readily.

The disadvantages are more numerous :—

The colour is generally not so fast against milling and rubbing, from which it appears that it is fixed more superficially than by the first method.

It is not very easy to dye to an exact shade; indeed, this can be done only after long experience. The method demands that the correct proportions of dyewoods required for any given shade be added to the bath before the saddening is effected, *i.e.*, at a stage when the colour of the wool gives little or no indication of the ultimate colour produced by the action of the mordant. Any misjudged proportions would make little difference if, after saddening, one could add with effect fresh quantities of one or other of the dyewoods still needed. This, however, is inadmissible, if economy of dye-stuffs is studied, because the mordant present in the bath not only prevents the extraction of colouring matter, but even tends to precipitate it within the dyewood itself, and in the liquor. It is evident, therefore, that it would only yield a useful effect after a large excess of dyewood had been added, and after this a further quantity of mordant would require to be added. As a rule, mistakes in "shading" of the kind mentioned are rectified, so far as new shades are concerned, by adding to the dye-bath small quantities of some very soluble colouring matter requiring no mordant—*e.g.*, Cudbear, Turmeric, or Indigo Extract—by which it is comparatively easy to obtain the exact tint required, since they at once dye the wool with their proper and only colour. With such dyestuffs, however, these last touches of colour put upon the wool do not generally possess the fastness against light, soap, and milling, of the fundamental colour.

The method gives rise in most cases to much loss of dyestuff, since the wool never absorbs the whole of the colouring matter, however prolonged the boiling with the dyewood before saddening may be, and all the colouring matter still unabsorbed is rendered insoluble and useless by the addition of the mordant or saddening agent. After saddening, the bath is thrown away, and the dense inky liquors and precipitates increase the pollution of the river or stream.

There are, indeed, many cases in which saddening in a separate bath does not quite yield such full colours as when a single bath is employed, since, even after the addition of the mordant or saddening agent, the dyeing still goes on to some extent, the colour precipitated in the bath not being entirely insoluble, especially in the presence of a slight excess of the mordant. Such is the case, *e.g.*, with Logwood and ferrous sulphate, Logwood and copper sulphate, Madder and potassium dichromate, Logwood and alum, &c.

222. The Single Bath Method.—As an example of the third or "one-dip" method of dyeing, in which the wool is dyed from the beginning with a mixture of colouring matter and mordant, one may quote the dyeing of cochineal scarlet. This method can be carried out only with those colouring matters and mordants which, when used together, yield precipitates somewhat soluble in the acid liquid of the bath, *e.g.*, Cochineal and stannous chloride, yellow dyewoods and alum or stannous chloride, Logwood and ferrous sulphate or copper sulphate, Madder and potassium dichromate, &c.

Although in all cases the colour is not quite so full and deep as that obtained by mordanting first and dyeing afterwards, it may still be sufficiently near the maximum intensity obtainable, to cause the process to be preferred in practice before any other, since it means, of course, a great saving in time, labour, and steam. In some cases, too, it gives a very much brighter colour than the other methods; the presence of the mordant in the bath prevents the impure extractive matters, tannic acid, &c., from becoming fixed on the wool. This action is very marked in the case of the yellow dyewoods when used with alum or stannous chloride. With Logwood and copper sulphate, ferrous sulphate, or alum, the full colouring power of the dyewood is not obtained, but, notwithstanding this, the method may be and is adopted in practice, the chief advantages gained being a saving of time and labour, and the requirement of less apparatus.

The "stuffing and saddening" method, and the "one-dip" method, are useful and economical whenever light colours are required, since in such colours the time and labour expended cost far more than the materials.

Sometimes, too, the light shades obtained by these methods are more uniform.

223. The Mordanting, Dyeing, and Saddening Method.—The fourth method mentioned, in which the wool is mordanted, dyed, and saddened, is adopted when it is desired to obtain the maximum fastness of colour, *e.g.*, in tweed-yarns. As an example of this method may be given, a fast black for the production of which the wool is first mordanted with potassium dichromate, then dyed in a fresh bath with Logwood, and finally saddened by passing through a fresh hot bath containing potassium dichromate. Another example is, the claret-brown produced by mordanting with potassium dichromate, dyeing in a fresh bath with Camwood, and saddening in the same bath with ferrous sulphate, towards the end of the operation. In these and similar cases, there is always a certain amount of the colouring matter which is merely absorbed by the wool, and not in combination with the mordant, and it is this uncombined colouring matter which the additional saddening fixes. Excess of mordant must be avoided, otherwise the colours on the wool are apt to have an unpleasant metallic lustre (they assume a bronzy, rusty appearance); especially is this the case with logwood and iron blacks.

Sometimes this additional mordanting operation has the object of modifying, and even brightening, the colour already on the wool. In such case the term saddening is inappropriate, and the operation is called "brightening" or "blooming." The agents used for this purpose are solutions of tin or alum.

224. Operations, &c., in Wool Dyeing.—Wool is dyed in all the various stages of its manufacture, namely, as unspun wool, slubbing (*i.e.*, the product of a preparatory stage of the spinning process), yarn, cloth, worn clothing, rags, and shoddy (*i.e.*, woollen rags torn up into flocks).

When the dyer receives it in the form of *raw-wool*, his first duty is to wash it well with tepid water, and then to scour it (*see* Wool Scouring), in order to remove all those natural impurities adhering to the fibre, which otherwise would seriously impede the entrance of the dye, and produce very unsatisfactory results.

If the wool is in the form of *slubbing*, or of *yarn*, the washing and scouring of the raw-wool have already been performed by the spinner, but in order to facilitate the spinning processes, and to prevent breaking of the fibre during the scribbling, &c., the scoured wool has been again impregnated with oil. The dyer must therefore first remove this by a second scouring process, if he desires to obtain the best results in dyeing.

From motives of economy, the scouring of slubbing and yarn is sometimes omitted, *e.g.*, in the case of low-class, cheap, carpet yarns, &c. Only experiment can show with what dyes such liberty can be taken with impunity, but in any case it is very irrational.

Woollen Cloth is sometimes sent to the dyer still saturated with the oil used by the spinner; sometimes it is already in an advanced stage of manufacture, having gone through the operations of scouring, milling, raising, cropping, pressing, and boiling; hence, a preliminary washing and scouring is or is not necessary, according to the stage in which the dyer receives the material.

Wetting-out.—In all cases, in whatever stage of manufacture the wool may be, it is essential that, previous to being introduced into the dye-bath, it should be thoroughly well "wetted-out" by a passage first through hot, then through cold water, and subsequent squeezing, in order to ensure ultimately an even or level dye, *i.e.*, that the colour shall penetrate each fibre regularly, and be uniformly diffused over the whole fabric. If wool were placed in the colour or mordant solution in the dry condition, the large quantity of mechanically-enclosed air would, for a time at least, prevent a proper and regular contact between the solution and the fibre, and an uneven, irregular dye would inevitably result.

Temperature of Dye-bath.—Generally speaking, the mordant or dye-bath is heated to the boiling point

Greater intensity of colour is thus obtained, owing to the softening of the substance of the fibre, the expansion of the external scales, and a more complete expulsion of air, all of which permit a readier entrance of the solution to the inner portions of the fibre. The employment of a high temperature becomes more necessary, the thicker and closer the texture of the material to be dyed, the less the liability to dissociation of the mordant, and the greater the insolubility of the colouring matter employed. In some cases, however, the higher temperature must be avoided, since it may be detrimental to the attainment of the brightest colour, *e.g.*, with Indigo Carmine, Magenta, Phosphine, Alkali Blue, Erythrosine, &c.

Level Dyeing.—Some colouring matters show a decided tendency to dye unevenly; with such, it is always advisable to introduce the material into the dye-bath at a low temperature, and then to raise the temperature very gradually to the boiling point.

When soluble colouring matters are employed, it is well to prepare solutions previously, and add them to the dye-bath already containing the necessary amount of cold or tepid water. Ground dyewoods, either loose or enclosed in bags, should be boiled in a bath about half full of water, the full complement of cold water being added afterwards, in order that the temperature may be suitably lowered previous to the introduction of the materials to be dyed.

Another method is to add the colouring matter to the dye-bath gradually, in which case the textile material should be withdrawn before each addition, unless the form of dye-bath renders this unnecessary.

A third plan, which proves to be efficacious, particularly when extremely soluble colouring matters are employed, is to add along with the colouring matter a certain proportion of some neutral salt, *e.g.*, sodium sulphate, common salt, &c. This addition renders the colouring matter somewhat less soluble, and hence it is absorbed by the wool more slowly. Above all, there must be a continual motion given to the textile materials during the mordanting and dyeing processes, so that each portion may be equally presented to the action of the mordant or colouring matter. This is effected either by hand or by machine.

The operations which follow the dyeing process vary according to the material and the colouring matters employed. In general, the loosely adhering dye-stuff is washed off, the excess of water is removed, and the goods are finally dried. Finishing processes are not considered in this manual.

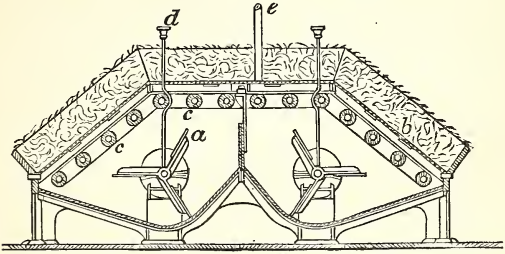


Fig. 67.—McNaught's Wool-Drying Machine (*Section*).

225. Unspun Wool.—*Dyeing Machinery.* The dye-vessel employed for loose-wool consists of a large open cylindrical cast-iron pan, similar to the indigo-vat shown on p. 305. It is provided with an emptying pipe below, covered with a sieve, beneath which enters also the steam-pipe for heating purposes. In many cases, direct fire heat is applied instead of steam, and for such large volumes of water as are usually employed in loose-wool dyeing the plan is economical. The stirring of the wool is effected by stout wooden poles, which are worked by hand. (Vacuum dyeing machines may also be employed.)

Washing Machinery.—Loose-wool is usually washed in the dye-vat, by running off the dye-liquor, refilling the vat with water, and stirring up the wool with poles, repeating the operation as frequently as may be necessary.

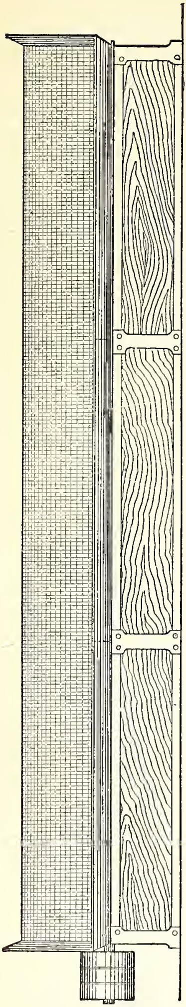


Fig. 68.—McNaught's Wool-Drying Machine (*Side View*).

The wool-scouring machine may also be used for washing (*see* p. 100). Before drying, loose-wool is passed through a pair of squeezing rollers, or the excess of water is removed by the hydro-extractor.

Drying Machinery.—The wool may be dried intermittently in an apparatus like that of McNaught, represented in Figs. 67 and 68.

It consists of a series of steam-pipes *c*, immediately above which the wool is spread out on a large surface of galvanised wire netting *b*. Beneath, in a box-like space, two ventilating fans *a* drive the heated air through the layer of damp wool. This may also be effected by means of a centrifugal fan. Steam is supplied by the pipe *e*; *d* is a tube for conveying oil to the bearings of the fans.

Loose-wool may also be dried in a continuous manner by Norton's machine, shown in Fig. 69.

The damp wool is placed on the feeding-apron A, and passed continuously, in zigzag fashion, through a hot-air chamber, by means of the endless bands B, C, D, E. The dry wool leaves the chamber at I. The fan F drives the external air, heated by the steam-tubes H, into the space J, and thence into the chamber; the moist air escapes by K; M and L are the inlet and outlet tubes connected with the steam-pipes H.

226. Woollen Yarn.—*Dyeing Machinery.* For yarn dyeing, the simplest apparatus is a substantially made, rectangular, wooden box A, about $\frac{3}{4}$—1 metre wide, and varying in length and depth to suit different quantities of material (*see* Fig. 70), also Fig. 45, p. 186.

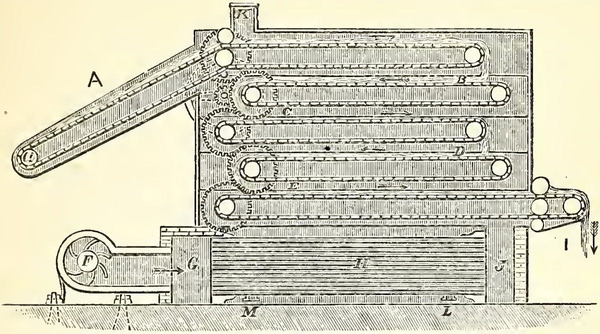


Fig. 69.—Continuous Wool-Drying Machine.

The water is heated by means of a perforated copper steam-pipe D, running centrally along the bottom. In the most complete arrangement, there is also a closed copper worm-pipe, so that the dyer may employ either

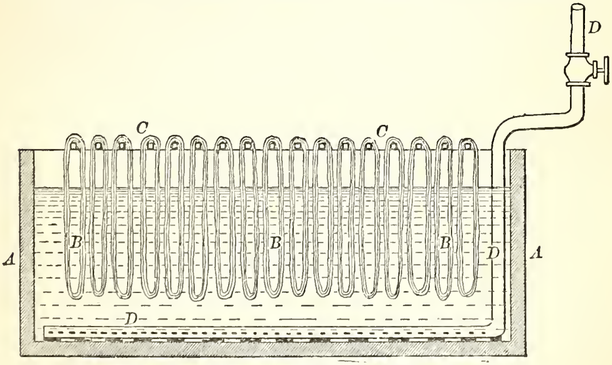


Fig. 70.—Woollen Yarn Dyeing Machine.

the one or the other in order to maintain the liquid at a constant level. Cold water taps for filling, and draw-off plugs, are conveniently situated.

The hanks of yarn B are hung on square wooden rods C, placed across the tank, and turned by hand, as described on p. 105 for yarn-scouring.

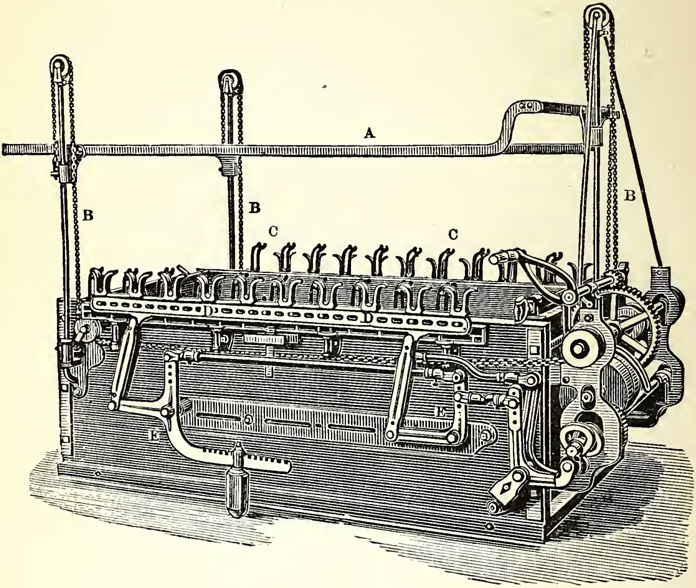


Fig. 71.—Pitt's Woollen Yarn Dyeing Machine.

An excellent example of a machine specially adapted for dyeing *woollen yarn* is that of Messrs. Pitt Bros., and illustrated in Fig. 71. The vat, which is of the ordinary kind, is provided with a light iron frame A resting upon the edges of three of its sides and beneath the ends of the rods of yarn. This frame can be moved up or down by means of the chains B, and thus the whole of the wooden rollers holding the yarn can be immersed in or removed from the vat liquor simultaneously. When the frame is lowered, the ends of the axes of the rollers rest in the sockets C fixed on each side of the vat. The turning of the hanks is effected by loose wooden blades, which are inserted within the loop of the hanks, and close to the supporting roller. The ends of these blades project and rest in a series of forks or notches fixed on horizontal rails D, situated on both sides of the vat. By means of a complicated system of levers E, actuated by a pair of cams, the rails D are moved both vertically and horizontally in such a manner that a small circle is described by the wooden blades which they support. Each blade is raised above the roller on which the yarn is suspended, then moves away from it, and then falls; the point of suspension of the yarn is thus being continually altered, and the yarn is drawn intermittently across the rollers. The movement of the yarn is indeed very similar to that which it receives when worked by hand, the difference being simply one of degree and not of kind.

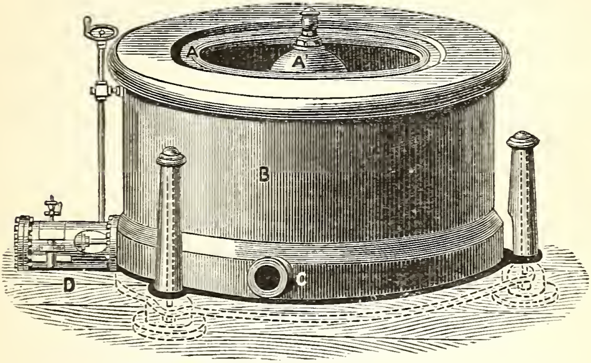


Fig. 72.—Hydro-extractor.

Washing Machinery.—Woollen yarn is washed by

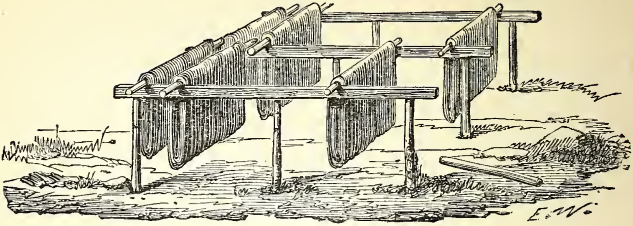


Fig. 73.—Arrangement for Drying Yarn in the open air.

hand in a rectangular wooden box, identical with that used for dyeing, or the rods full of yarn are placed under a perforated wooden drainer, where they receive a shower bath.

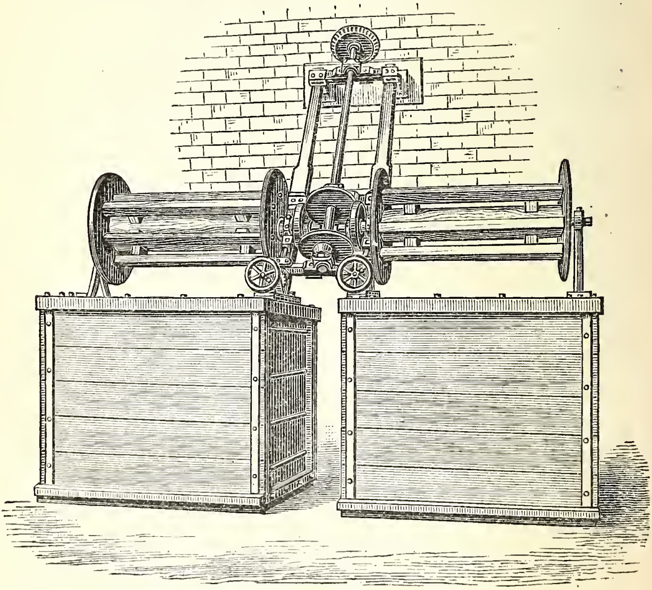


Fig. 74.—Pair of Winch Dyeing Machines for Cloth.

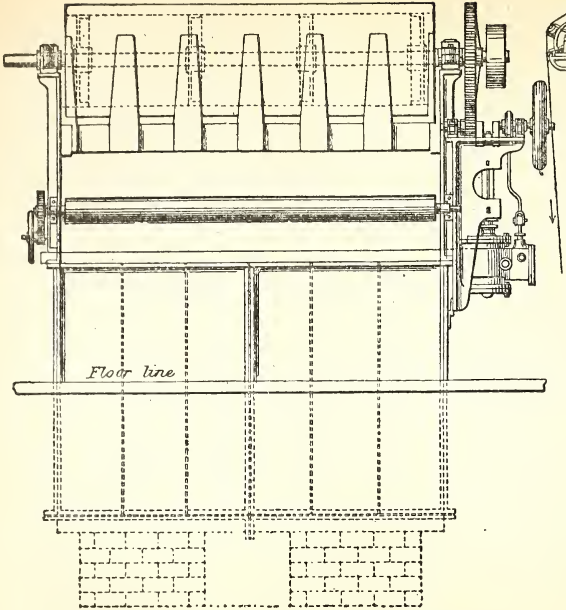


Fig. 75.—Union Cloth Dyeing Machine (Front Elevation).

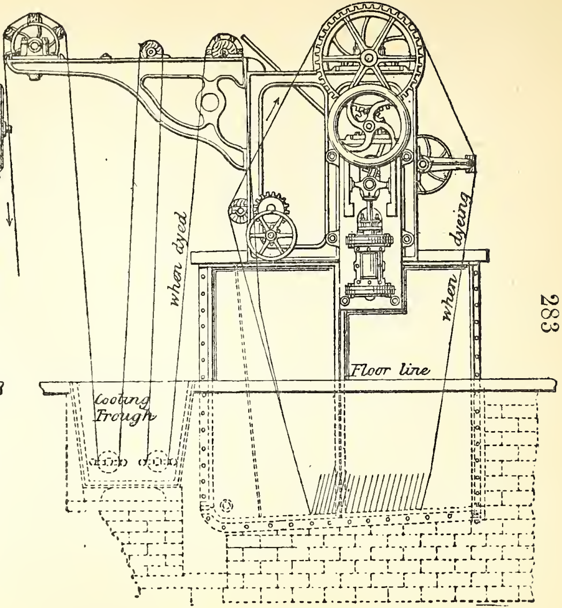


Fig. 76.—End Elevation of Fig. 75.

Excess of water is removed from woollen yarn by means of the hydro-extractor (Fig. 72). That made by T. Broadbent & Sons consists of a drum or cage of galvanised or copper wire-work A A′, so supported that it can be made to revolve, by means of an engine, very rapidly (*e.g.*, 1,500 revolutions per minute), with a perfectly smooth movement. The cage is enclosed in a suitable cast-iron casing B. The wet yarn is placed as evenly as possible in the cage to balance it. The water is expressed by the powerful centrifugal force developed during the revolution of the cage, and makes its exit by the pipe C.

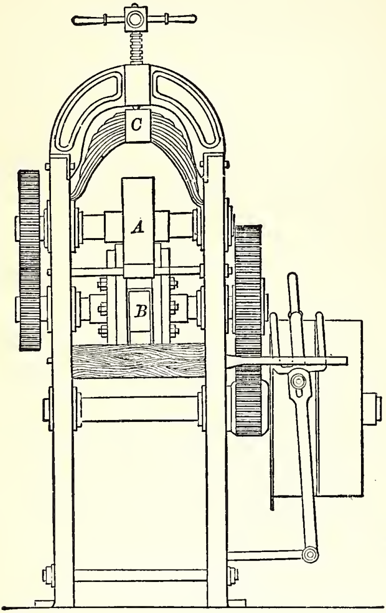


Fig. 77.—Woollen Cloth-Squeezing Machine.

Drying.—Woollen yarn is dried in stoves, or in the open air, as shown in Fig. 73.

227. Woollen Cloth.—*Dyeing Machinery.* Woollen cloth, like yarn, is dyed in a rectangular wooden vat. In the better forms of apparatus, a perforated wooden partition divides off a small portion in front, into which dyewares, &c., can be added without necessitating the removal of the goods from the dye-liquor; the perforated steam-pipe for heating is also situated at the bottom of this compartment. After introducing the pieces, they are stitched end to end, to form an endless band; this is supported, and drawn continuously through the liquor by means of reels or winches placed above, and driven by power.

Fig. 74 gives a perspective view of an arrangement by W. Kemp, of Leeds. During the movement of the pieces, it is the special duty of an attendant to see that any knots which may be formed are as speedily as possible unloosed. Each dye-vat usually contains several pieces of cloth.

Figures 75 and 76 represent the dye-vat usually employed for dyeing unions (cotton and wool). The vat is made of iron, and divided across into several compartments by means of perforated plates. This arrangement prevents intermingling and entanglement of the several pieces, of which there may be from forty to eighty, each about forty-five metres long, and so stitched as to form six or eight endless bands.

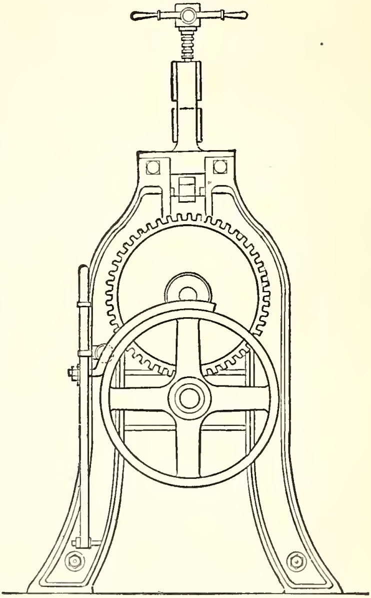


Fig. 78.—Side View of Fig. 77.

The winch of each dye-vat is driven by means of a small engine attached to the machine.

Washing Machinery.—The machine generally used for washing woollen cloth is the "dolly" (*see* p. 106).

In some cases the wash-stocks (Fig. 52) may be used with advantage, *e.g.*, when the material is very thick and heavy.

Washing in the open width may be done by the open-scouring machine (Fig. 37, p. 109).

Figs. 77 and 78 represent a woollen cloth-squeezing machine in which the water is expressed by a brass roller B, in the groove of which a disc roller A is pressed by a strong spring C.

Drying Machinery.—Drying is effected by means of the drying machine shown in Fig. 79.

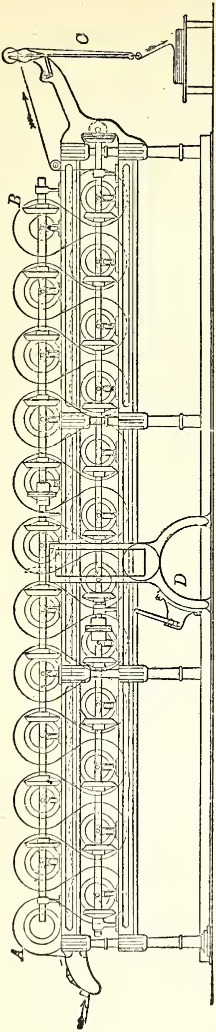


Fig. 79.—Cylinder Drying Machine.

This machine consists of a number of hollow copper or galvanised iron cylinders A B, heated by steam and driven by bevelled gearing and an engine at D. The axes of the cylinders are hollow, the steam entering at one end, the condensed water escaping by the other. A folding arrangement C is attached at the end of the machine.

Another mode of drying is by means of the "tentering" machine, of which there are several varieties.

Fig. 80 shows one of the most generally used arrangements, by W. Kemp & Co., Leeds. It consists of a series of horizontal steam-pipes C C, supported by iron framing, between which the cloth is led in a zigzag course and stretched condition. The cloth is introduced at A, and guided by means of two endless chains B B, furnished throughout their length with pins, on which the selvedges of the cloth are pushed down by revolving brushes as it enters the machine. As the dried cloth leaves the machine it is folded down mechanically at E.

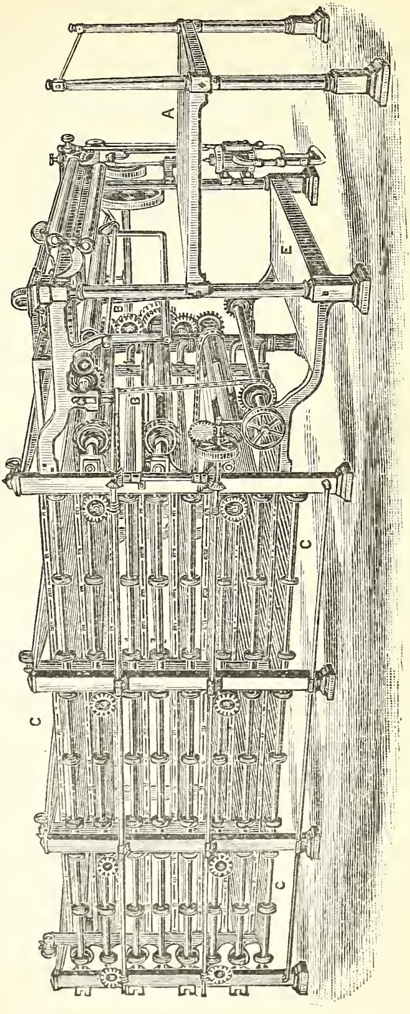


Fig. 80.—Tentering Machine.

228. Irregular Dyeing.—A very marked feature in the dyeing of woollen materials, and one to be well borne in mind, is, that after they are removed from the dye-bath, and so long as they contain the hot liquor of the bath, the dyeing process still continues. The wool, or the mordant in union with it, continues slowly to attract such colouring matter as remains dissolved in the absorbed dye liquor, and the material becomes somewhat darker in colour. It seems as though the wool had an insatiable appetite for the colouring matter, and the material is said to "feed."

If due care is not taken, this tendency may lead to an uneven shade in the ultimate colour of the material, however well the operation of dyeing proper may have been done. If, for example, the woollen cloth, yarn, or fibre is removed from the dye-bath and at once thrown on the floor to form there an irregular heap, this residual dyeing or "feeding" goes on in an irregular manner. The same takes place in recently dyed yarns or pieces which are hung on poles or over rails; the hot dye-liquor drains to the lowest portion, and there causes a darker shade of colour to result.

The best mode of obviating this possible defect, is to remove the source of heat, and allow the material to cool slowly in the dye-bath, at the same time continuing the regular movement of the material. In this manner the "feeding" is made to proceed in a regular manner. In practice this takes too long, and hence it is customary to cool the dye liquor more rapidly by running into it the necessary amount of cold water, in which case the deepening of colour is also somewhat diminished.

Another method of preventing irregular dyeing arising from this cause, is to wash the materials immediately after they have been withdrawn from the dye-bath. This of course prevents all danger of "feeding," and possible irregularity in colour, but the shades obtained when this method is adopted are not usually so full and rich as in the first method. They look paler, and the nap or loose fibres may, in some cases, be almost entirely devoid of colour, giving the material a very unsatisfactory grey appearance, as if it were insufficiently dyed.

229. Dyeing in the Wool, Yarn, and Piece.—The quality of the wool has considerable influence upon the depth and beauty of colour ultimately obtained.

Coarse, hard wool, and such as possesses more the character of hair—*e.g.*, worsted, alpaca, mohair, &c.—dyes less readily than fine wool having the merino character. The finer the wool the greater will be the quantity of colouring matter which it will take up, and the richer and more brilliant will be the colour one is able to impart to it. No doubt this is owing to its greater porosity, its softer and more absorbent character, and the less horny character of its scales.

If in any dyed woollen fabric the colour has been imparted to it while it was yet in the state of unspun wool, it is said to be *wool-dyed*, or to have been *dyed in the wool.* When the dyeing took place while it was in the state of thread or yarn, it is said to be *yarn-dyed*, and when it was not dyed until it had become woven cloth, it is said to be *piece-dyed.*

Wool-dyed cloth is generally the most esteemed, because the dye chosen must be fast, since it has to withstand all the subsequent manufacturing operations. Then, again, each individual fibre being, as it were, separately dyed, the material is uniformly dyed throughout, however thick it may be; and if the colouring matter is of a permanent character, the cloth will preserve its colour in spite of wear and tear.

Wool-dyeing is preferred for dark-coloured goods, and such as have to bear much friction. It is rarely used for light colours, since these would be soiled during the subsequent manufacturing operations.

When the fabric is not of one uniform colour, but is composed of threads of different colours—*e.g.*, in Tweeds, Kidderminster carpets, shawls, &c.—either wool-dyeing or yarn-dyeing, of course, becomes a necessity. In such cases, where the great desideratum is to have large quantities of yarn of a very uniform shade, wool-dyeing or slubbing-dyeing is preferred to yarn-dyeing, for even if the loose-wool or slubbing be somewhat unevenly dyed, the subsequent operations of scribbling, carding, &c., equalise most thoroughly any irregularity of colour.

Wool-dyeing must also be adopted in the manufacture of "mixed yarns," such yarns, namely, as are spun with a mixture of variously-coloured wools.

Wool-dyeing is generally adopted by those yarn or cloth manufacturers who wish to do their own dyeing.

Piece-dyeing is preferred for light colours and such as are of a fugitive character, though it by no means follows that all piece-dyed goods are dyed with loose or fugitive colouring matters. Such a fast and permanent colour as vat-indigo-blue is as frequently applied by piece-dyeing as by wool-dyeing.

Piece-dyed goods, especially such as are made of hard-spun yarns, or are closely woven, thick, or well-milled, are sometimes apt to become grey with wear and tear, even if the colouring matter applied has all the requisite permanency desirable. This arises from the fact that the central part of the fabric has remained more or less undyed, and through wear becomes partially exposed. Piece-dyeing may often be detected by tearing the fabric and ascertaining whether the centre is fully dyed or not. In some cases, particularly with light, bright colours—*e.g.*, scarlets on hunting-cloths—an increased brilliancy of the colour is produced by piece-dyeing, since the central white shines through the surface colour. In such cases there is considerable economy in colouring matter by piece-dyeing.

The same remarks apply in a lesser degree to yarn-dyed goods.

Yarn-dyeing and piece-dyeing form, generally, distinct branches of trade.

For the production of a given shade, the largest amount of colouring matter is required in wool-dyeing; somewhat smaller amounts may be taken in yarn-dyeing, and in piece-dyeing, less still.

Piece-dyed goods, if composed of one kind of fibre only, are necessarily of one uniform colour. When, however, the fabric consists of two fibres—*e.g.*, of cotton warp and woollen weft—although the goods may be piece-dyed, they may have every appearance of having been yarn-dyed, since each fibre having a different power of attracting the colouring matter, has acquired a different tint. In some cases one fibre may remain altogether undyed, this is so, for example, with the cotton when such a mixed fabric has been dyed in an acid bath with Cochineal, Indigo Carmine, &c. In other cases the difference in colour between the two fibres is still further increased by submitting the fabric to two distinct processes of dyeing, the one being intended for the wool, the other for the cotton ; the fabric may, indeed, be doubly piece-dyed, and yet contain two such distinct colours as, say, black and red. This method of dyeing is, however, frequently employed when mixed fabrics of cotton and wool are dyed one uniform shade if it is not possible by a single dyeing operation to give exactly the same tint to the two fibres.

230. **Matching-Off.**—The immediate object which the dyer has in view, is to dye a quantity of textile material so that the whole of it shall have a definite shade of a given colour, similar, it may be, to that of a pattern supplied by the merchant, or otherwise presented to him. His skill consists in knowing exactly which mordants and dye-stuffs to employ, also their relative and absolute proportions, and to determine the temperature and duration of the mordanting and dyeing processes, in order to ensure the result aimed at. Even though the pattern-colour may have been originated by the dyer himself at some previous period, he dare not implicitly rely on obtaining exactly the same result by simply repeating his former trial in every detail. The reason of this lies in the fact that the quality of the dye-wares and of the fabric may have varied meanwhile. It is also a fact well known to practical dyers, that different qualities of wool—*e.g.*, merino and English wools—have different powers of attraction for colouring matter, so that, when dyed under exactly the same conditions, marked differences in colour result. Even in wools which are more closely related to

each other than the two just mentioned, similar differences are observed (*see* p. 289).

With regard to the irregularity occurring in dye-wares, it is very marked in the natural colouring matters or dyewoods. Their colouring power may, indeed, vary each year, unless they are mixed and made equal to a standard sample by the merchant or dyewood cutter. For such reasons, therefore, and perhaps because of others of a more subtle nature, it is necessary, in order to judge of the progress of the dyeing, that the dyer should occasionally compare, with the sample pattern, small portions of the wool, yarn, or cloth, taken from the bulk in the dye-bath. In the case of cloth, these small portions are either cut from the ends of the pieces themselves, or from some small odd bits of the same kind of material which have been specially attached for the purpose.

Before making the comparison, the " swatch, " " fent," or " trial-bit " taken from the dye-bath must be dried, by which it assumes a much lighter or paler appearance; it is then placed by the side of the sample pattern, and the two are examined and compared by reflected light, being held at some little distance from the eye, and with the back of the observer to the light.

They are then compared " overhand." To this end the two samples are placed between the light and the observer, who then glances along the surface, in order to catch the light transmitted through the projecting fibres. A judgment must be formed immediately, otherwise the eye soon becomes fatigued, and incapable of discerning nice differences of shade.

Sometimes the eye becomes tired through comparing or " matching off " a large number of different swatches of the same bright colour, in which case relief and increased power of discernment are most rapidly gained by occasionally gazing steadily for a few seconds at a piece of cardboard or other material possessing the complementary colour of the samples under comparison. In comparing reds, for example, the eye is relieved by looking at green, if blues by looking at orange, and *vice versâ*.

Having made the comparison of trial-bit with sample-pattern, the dyer judges whether the desired colour has been arrived at or not. In the latter case, if the tone of the colour is right, but it lacks intensity, the dyeing is either simply prolonged, or a further addition is made, of each colouring matter in the relative proportions already employed.

If the colour lacks the proper tone the dyer then adds one or other of the dye-stuffs already employed, in such amount as he considers necessary to correct the error.

Sometimes a difficulty is found in obtaining the exact tint or brilliancy required by simply using the dyewares decided upon in the first instance, and it may be necessary to make some slight addition of other colouring matters, which it was not originally intended to use. This is frequently a sign of want of experience, but it may also arise from some unexpected change in the quality of the dyewares or the textile material, or from some other cause.

In dyeing to shade, the young dyer is recommended to err on the side of employing a deficiency of colouring matter rather than the reverse, since he can readily make further additions, but cannot very well correct the defect arising from the use of an excess of dyeware.

It is well to bear in mind, too, particularly with the polygenetic colouring matters, that the affinity which any given mordant has for colouring matter varies with the different colouring matters. When, for example, a dyeing operation is nearly completed, but it has been found necessary to add a further quantity of some one particular dyewood, the change in shade thus produced is not always simply due to the addition of the colour proper to the dyewood, but also to a partial displacement of some one or other colour already on the wool.

The yellow colour of aluminium-mordanted calico, dyed with Quercitron Bark, is displaced by dyeing with

Logwood, and the purple colour thus produced is again displaced, and changed to red by dyeing with Madder.

In matching-off, care should be taken to have, if possible, a north light, not only because it is steadier, but because there is an absence of that excess of yellow light always present in the more direct rays of the sun; these greatly modify the aspect of colours, and render comparison more difficult. For the same reason it is impossible to judge accurately of the true shade of a colour by gas-light. This defect is partly overcome by using spectacles of plain glass tinted slightly blue.

Many practical dyers have long been in the habit of matching-off at night by means of the magnesium light, and in recent years the electric arc light has been used for the same purpose.

Although colours more nearly assume their normal tint under these lights, they are by no means identical in character with those exhibited under ordinary sunlight. There is, indeed, in both these artificial lights an excess of blue or purple rays, and for accurate colour-matching the light should be screened with globes of tinted glass. The correct tint to employ may be determined by a spectroscopic examination of the light.

NOTES ON SILK-DYEING.

231. With few exceptions, the general method of dyeing silk is similar to that employed for wool. By far the largest amount of silk is dyed with coal-tar colouring matters, which do not require the aid of a mordant; at most, some assistant—*e.g.*, acid, soap, &c.—is needed, and the dyeing usually takes place in a single bath. Sometimes, however—specially in the case of black dyeing—two or more baths are employed, and, indeed, the whole process becomes more complicated than most methods of dyeing employed for any fibre.

The silk-dyer uses comparatively little machinery, and being most of it intimately connected with special operations, allusion is made to it when referring to these.

APPLICATION OF THE NATURAL COLOURING MATTERS.

CHAPTER XIII.

BLUE COLOURING MATTERS.

INDIGO.

232. Theory of Indigo Dyeing. — This valuable colouring matter is obtained from the leaves of various species of *Indigofera* (*I. tinctoria*, *I. disperma*, *&c.*), which are cultivated largely in India. The method *par excellence* employed in dyeing with Indigo is founded on the property it possesses of being converted under the influence of reducing agents (*i.e.*, bodies capable of yielding nascent hydrogen) into indigo-white which is soluble in alkaline solutions. When textile materials are steeped for a short time in such solutions, and then exposed to the air, they become dyed blue in consequence of the re-oxidation of the indigo-white absorbed by the fibres, and the precipitation of insoluble indigotin thereupon, and, indeed, in such a manner as to be indelibly fixed. This "indigo-vat" method is applicable to all textile fibres, and gives permanent colours.

Another method of dyeing with Indigo, but one which yields fugitive colours, and is applicable only to the animal fibres, depends on the fact that Indigo treated with strong sulphuric acid becomes changed into soluble indigotin-di-sulphonic acid (Indigo Extract). Animal fibres attract and are dyed with this compound when they are simply steeped in its hot and slightly acidified solutions.

Vat-blue is largely employed, particularly in woollen dyeing, as the blue part of compound shades, *e.g.*, browns, drabs, &c. The same may be said of Indigo Extract or Indigo Carmine blue, with regard to wool and silk dyeing. Indeed, this colouring matter possesses certain advantages over the majority of blue colouring matters. It can be associated with other acid colouring matters, and it dyes very level shades. Its only drawback is its extremely fugitive character.

233. Indigo Grinding Mills.—One of the first necessities in employing Indigo in dyeing is to have it

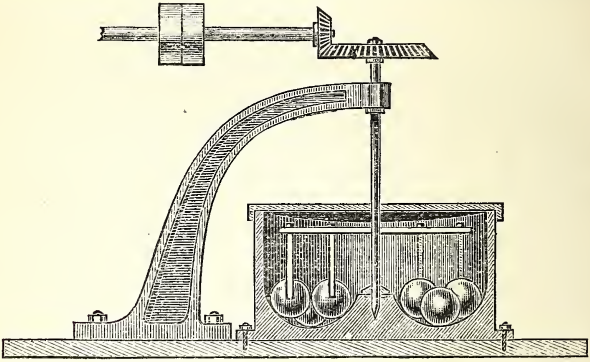


Fig. 81.—Indigo Grinding Mill.

thoroughly well ground. When required for making Indigo Carmine it must be ground in the dry state, but for the indigo-vat it may be mixed with water, by which means the grinding is considerably facilitated.

The oldest form of grinding machine is the stamping mill, provided with an arrangement for passing the ground Indigo through fine sieves. At present the mills generally employed consist of cast-iron vessels, in which the Indigo is ground either by the rolling of heavy cannon balls, or of iron cylinders. The ball mills are said to give the finest powder; the cylinder mills the greatest yield within a given period. Fig. 81 represents a section of one of the best forms of ball mills. It consists of a strong iron box enclosing several heavy cannon balls, which are pushed round by means of a pair of revolving arms. Sometimes the bottom of the box is flat, and heavy blocks of sand-stone are substituted for balls.

234. *Application to Cotton.*—The fermentation vats so much used in dyeing wool with Indigo, are never employed for cotton, since it is essential that it should be dyed in the cold to obtain the best colour; and, further, it permits the use of vats, in which the reduction of the indigo is effected in a manner more under control. According to the reducing agents employed, the indigo-vats used for cotton may be named as follows: the *ferrous sulphate vat*, the *zinc powder vat*, the *hydrosulphite vat.*

235. **Ferrous Sulphate Vat.**—This vat, usually known by the name of the *lime and copperas vat*, is the oldest, and perhaps the one still most commonly employed. The vats or dye-vessels are rectangular tanks of wood, stone, or cast-iron. The size varies according to the material to be dyed; for calico they are generally two metres (6½ ft.) deep, two metres long, and about one metre broad, while for yarn-dyeing they are somewhat smaller.

In order to economise the Indigo as much as possible, the vats are generally worked in sets of ten.

The materials used in preparing this vat are:—

	Cloth.		Yarn.
Water	4,000 litres	or	750 litres.
Indigo	40 kilos.	„	4 kilos.
Ferrous sulphate	60--80 „	„	6–8 „
Slaked lime (dry)	50–100 „	„	5-10 „

The chemical changes which take place during the "setting" or preparation of the vat may be briefly summed up as follows. The lime decomposes the ferrous sulphate, and produces ferrous hydrate, which in the presence of the indigo rapidly decomposes the water, and becomes changed into ferric hydrate, while the liberated hydrogen at once combines with the indigotin to form indigo-white. This last substance combines with the excess of lime present, and at once enters into solution. These reactions may be expressed by the following chemical formulæ :—

$$\underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Lime.}}{Ca(OH)_2} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Ferrous hydrate.}}{Fe(OH)_2}.$$

$$\underset{\text{Ferrous hydrate.}}{2[Fe(OH)_2]} + 2H_2O = \underset{\text{Ferric hydrate.}}{Fe_2(OH)_6} + H_2.$$

$$\underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + H_2 = \underset{\text{Indigo-white.}}{C_{16}H_{12}N_2O_2}.$$

The order in which the ingredients are added is of comparatively little moment, and varies with different dyers. The most rational method, however, is to fill the vat with water and add first the ground Indigo and milk of lime; after raking up well, a solution of ferrous sulphate is added, and the whole mixture is systematically raked up at frequent intervals during twenty-four hours, until the Indigo is thoroughly reduced. With this plan, the actual reducing agent, ferrous hydrate, is always in the presence of an excess of Indigo, and the indigo-white the moment it is produced is dissolved in the excess of lime. Owing to the mixture becoming rapidly thick and difficult to stir well, the more usual plan adopted is to put in the Indigo and ferrous sulphate first, and to add the milk of lime gradually. Lime is used in preference to caustic soda because the vat thus produced dyes the cotton more readily; and owing to the film of calcium carbonate which forms on its surface, the indigo-white in the liquor beneath is less liable to become oxidised.

The ferrous sulphate employed should be as pure as possible. Any admixture of copper sulphate is injurious because of its oxidising influence, while the presence of aluminium sulphate and basic ferric sulphate, since these are quite inert as reducing agents, causes loss of so much lime as is required for their decomposition, besides a useless increase of sediment. The use of a large excess of ferrous sulphate and lime should also be avoided for this last reason. Ferrous sulphate, containing copper sulphate and ferric sulphate, is readily purified by boiling its solution with iron turnings, whereby the copper is precipitated, and the ferric sulphate is partly reduced to ferrous sulphate, or fully decomposed and precipitated.

A freshly made-up vat is in good condition when numerous thick dark-blue veins appear on raking up the liquor, and the surface becomes rapidly covered with a substantial blue scum or "flurry." The liquid should be clear, and of a brownish-amber colour; if greenish, it shows the presence of unreduced Indigo, and requires a further addition of ferrous sulphate. If the colour is very dark, more lime is required.

At the end of every day's work the vats should be well raked up, and, according to their appearance, "fed" or replenished with small additions of lime and ferrous sulphate. The rake used for this purpose consists of a rectangular iron plate, with long wooden handle attached.

Before dyeing, the flurry should be carefully removed with an iron scoop or "skimmer," otherwise it attaches itself to the cotton, and causes it to look uneven or spotted.

Cotton yarn should be previously well boiled with water, in order to make it dye evenly. When dyeing light shades of blue, only a few hanks are dyed at once, the dipping, turning, and squeezing being performed with the utmost regularity. According to the depth of blue required, the duration of each immersion may vary from one to five minutes or more, and after wringing, the hanks are thrown aside, and allowed to oxidise completely.

The amount of indigotin which is precipitated on the cotton is said to vary with the duration of the immersion; if this be true it would appear that the cotton really attracts indigo-white from the vat solution, and is not dyed merely by reason of the indigotin precipitated from the portion of liquid absorbed by the fibre. The most economical method is to dye the cotton first in the weaker vats, and then to pass it through each succeeding stronger vat until the desired shade is obtained. For a dark shade, the cotton should not be put at once into a strong vat, because it would be difficult in this way to obtain even colours; and in the long run, the method would not be so economical. For light shades of blue, only a few of the weaker vats are needed.

By this plan of always using the weakest vat first, so long as it yields any colour, each vat in turn becomes thoroughly exhausted.

After dyeing, the carbonate of lime which is deposited on the fibre is removed by rinsing in sulphuric acid, 2°—4° Tw. (Sp. Gr. 1·01—1·02). This operation removes the grey tint, and brightens the colour considerably. The cotton is finally dyed in a moderately strong vat, wrung out and dried at 60° C. This imparts to it the coppery lustre so much admired. It is, however, entirely superficial, and may be removed by simply washing in water.

As a rule, however, washing is avoided, since the indigo is apt to rub off, and the colour may look bare and wanting in body and intensity. Vat blues are improved in colour by passing the goods through lime-water or a hot soap bath, probably because of the removal thereby of some yellow colouring matters.

When dyeing *cotton cloth* or *calicoes*, the dry pieces are fastened by the selvedges on a rectangular wooden frame, having small brass hooks at the top and bottom; they are stretched moderately tight, and each fold is perfectly free. When filled the frame is alternately dipped beneath the surface of the vat liquor for fifteen to twenty minutes, and then raised above the vat by means of ropes and pulleys, in order to expose the calico to the air, so that indigotin may be regenerated and precipitated on the fibre. During the immersion it is customary to stir the liquor gently by means of a "muddler," *i.e.*, a short-handled rake having a wooden head.

Another method of dyeing calico, sometimes called "skying," because used for light blues, is shown in Fig. 82.

The pieces are passed through a series of rollers, arranged on a wooden frame immersed in the vat A. At the point of exit they pass through a pair of squeezing rollers, and are then led over a similar system of rollers B, outside the vat, for the purpose of oxidation. The whole process may be repeated two or three times, according to the intensity of colour required.

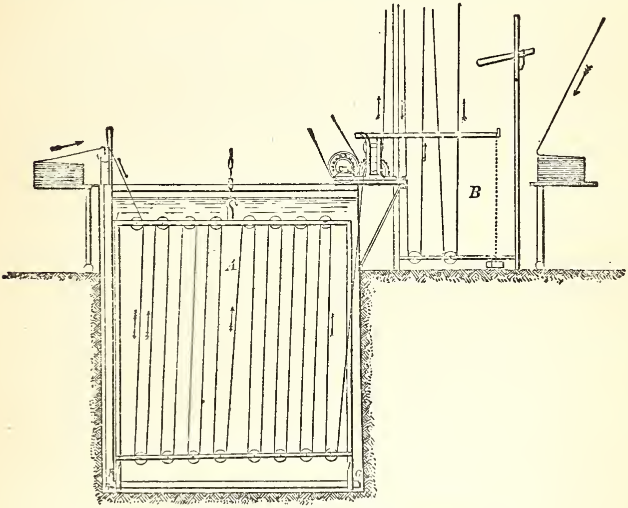


Fig. 82.—Continuous Indigo Dyeing Machine.

After leaving the vat, the pieces are first rinsed in cold water, to remove the loose lime and Indigo adhering superficially, and then in dilute sulphuric acid, 4°—8° Tw. (Sp. Gr. 1·02—1·04), to dissolve off the calcium carbonate; they are finally washed and dried.

All the indigo washed-off in the rinsing pits, as well as the sediment of the vats themselves, must be collected in special tanks, in order to recover the indigo.

According to F. C. Calvert, the vat sediments consist largely of an insoluble compound of indigotin and ferrous oxide, forming a bulky flocculent green precipitate. From this the indigotin can be recovered by decomposing it in the cold with strong hydrochloric acid.

Another method is to mix the vat sediments with water, and boil with some cheap, energetic reducing agent, *e.g.*, with caustic soda and orpiment. After settling, the clear liquid is drawn off, and oxidised by pumping it into a trough which stands at a high level, and allowing it to flow into a large tank; here the precipitated indigotin is washed and collected.

By adopting such methods of recovery, the total loss of Indigo may be reduced to 2—3 per cent. of the original weight employed.

It is sometimes the custom to dye the cotton or "bottom" it with catechu brown, manganese bronze or brown, or a blue shade of aniline black, previous to introducing it into the indigo vat. By this means, very deep blue shades can be obtained with less indigo than would otherwise be required.

It is well to remember that when aniline black is used the colour may be liable to become green on exposure.

In order to add a fictitious purple bloom or rich effect to the colour, vat blues are sometimes dyed afterwards or "topped" in a dilute solution of Methyl Violet or Methylene Blue, and dried without washing; less frequently, they are dyed a logwood blue.

236. Zinc Powder Vat.—This vat is frequently used on the Continent, and also in Great Britain. It is founded on the fact that zinc in the presence of lime and Indigo readily decomposes water, and combines with its oxygen, whilst the liberated hydrogen reduces the indigotin to indigo-white, which is at once dissolved by the excess of lime present.

$$Zn + H_2O = ZnO + H_2.$$

The relative proportions used of the several ingredients vary according to their quality, especially as regards the Indigo employed.

The following may be considered as average amounts:

Water	4,000 litres
Indigo	40 kilos.
Zinc powder	20 ,,
Slaked lime	20 ,,

The whole is well stirred occasionally during eighteen to twenty-four hours, when it is ready for use. Lime and zinc powder are added as occasion requires. It is an extremely simple vat, easy to work, and possesses even certain advantages over the "lime and copperas" vat. In the first place, the sediment is reduced to about one-seventh of that in the vat referred to. Then the absence of ferrous sulphate removes the possibility of the formation of the insoluble compound of indigotin with ferrous oxide referred to on the previous page.

Hence this vat can be used for a much longer time without emptying, than the "lime and copperas" vat, and there is little or no loss of Indigo.

Its chief defect is that it is liable to be muddy and frothy, from a continuous slight disengagement of hydrogen gas. No hydrogen is given off, however, until the whole of the indigo is reduced, so that *much* froth denotes the presence of excess of zinc. If there be only little froth, it is removed by vigorously stirring up the vat several times, and then allowing it to settle, but with a large excess, a further addition of Indigo should be made before stirring. After settling for an hour, the vat should be sufficiently clear for dyeing.

If the vat is muddy, the same remedy must be applied, since the cause is the same. It is of no use to let it stand for a long time in the hope that it will settle; the hydrogen simply accumulates, and the liquid becomes more muddy still. The liquid must be vigorously stirred up, in order to liberate the hydrogen from the sediment.

The dyeing should be completed before the liquid has had time to become muddy again. Experience alone can teach the exact amount of zinc powder which should be used, so that the vat may be maintained in an effective condition, yet free from the defects mentioned.

Some dyers find it an advantage to add about 12—20 kilos. of iron borings. These act mechanically, by presenting a large and rough surface, from which the hydrogen gas is more easily liberated, and thus a clear vat is more readily obtained.

237. **Hydrosulphite Vat.**—This vat is prepared for cotton exactly in the same way as for wool (*see* p. 308). The cotton, however, should be dyed in a cold solution.

238. *Application to Wool.*—In order to utilise the Indigo to the fullest extent, it is previously ground with the addition of water, and added to the dye-vessel in the form of a fine smooth paste. The "vat" or dye-vessel in which the reduction of the indigo and the dyeing takes place, is a large tank, generally made of cast-iron (about 2 metres wide and 2 metres deep). For dyeing unspun wool it is generally round, for piece-dyeing, square. The whole is enclosed in brickwork, so arranged that the upper portion of the vat is surrounded by a chamber or canal, into which steam can be admitted. By this means the liquid of the vat is heated from the outside, and a regular temperature can always be maintained, without any danger of disturbing the sediment.

During the "setting" of the vat the contents are stirred up, either by hand, by means of a rake, or by a mechanical arrangement fixed in the bottom of the vat, and driven by machinery. Before dyeing, the contents are allowed to settle, since the textile material must always be dyed in the clear liquid. The disturbing of the sediment is prevented as much as possible by suspending in the vat, 1 metre below the surface, a so-called "trammel," *i.e.*, an iron ring or frame, across which coarse rope network is stretched.

The accompanying figure (Fig. 83) gives the section of a well-arranged round indigo-vat for wool dyeing, with mechanical stirrer, &c. A is the steam-chamber surrounding the vat, B the steam-pipe for heating it, J the trammel-net, I the emptying-pipe ; D is a fixed bar supporting the stirring-screw C and the cone E. The parts drawn in dotted lines represent the movable portions of the stirring arrangement ; G is a strong wooden bar which can be readily fixed across the top of the vat ; it supports a pair of cog-wheels, and the fast and loose pulleys H ; F is a vertical connecting-shaft, which by reason of the guiding cone E can be readily connected with the screw C. A cheaper but less substantial arrangement is that in which the vat is made of wood, and heated internally by a copper steam-pipe forming a spiral half-way up the walls of the vat. When not in use for dyeing, and to prevent loss of heat and oxidation of the reduced indigo, the vat is covered with a wooden lid, which is divided into two or three pieces, for the sake of convenient handling. It is often the custom to throw over it a woollen cloth cover in addition. According to the materials used in

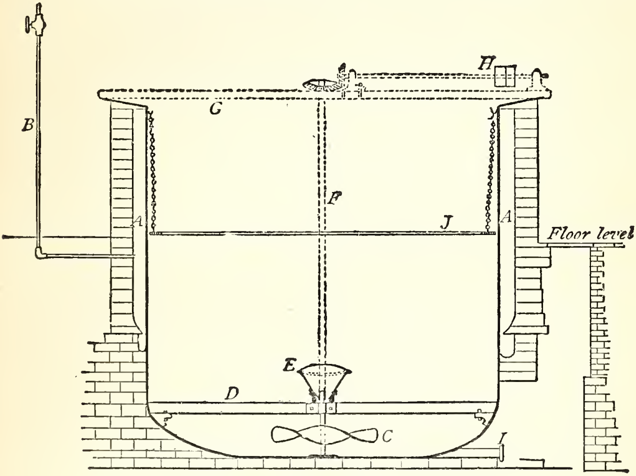


Fig. 83.—Woad Vat.

preparing or "setting" a vat for woollen dyeing, the following kinds may be distinguished: the *woad vat*, *potash vat*, *soda vat*, *urine vat*, and *hydrosulphite vat*.

239. Woad Vat.—In setting this vat, the following substances are employed for a vessel of the dimensions already given: Indigo, 15 kilos.; woad, 300 kilos.; bran, 10 kilos.; Madder, 2—15 kilos.; dry slaked lime, 12 kilos. The vat is first partly filled with water, the crushed woad is then added, and the whole is well stirred up and heated to about 50°—60° C. This temperature is maintained for twenty-four to thirty hours, the stirring being repeated at intervals during the first two hours. The well-ground Indigo, also the bran, Madder, and about half the total quantity of lime, are now added; after well raking up the whole mixture, the vat is covered over, and left to itself for twelve to twenty-four hours.

By this time fermentation has generally well begun. It is recognised by the following appearances: the surface of the vat-liquor becomes covered with a coppery-blue scum or "flurry." On gently stirring the liquor, it is seen to possess a greenish-yellow colour, interspersed with blue veins or streaks of regenerated indigo, and the general odour of the vat is agreeable. If the bottom of the vat liquor is disturbed, a slight froth appears on the surface, and on bringing up a portion of the sediment with the rake, it shows evidences of being in a state of slight fermentation, and smells somewhat sour. A piece of wool immersed in the liquid for a short time, and then exposed to the air, becomes dyed blue. All these appearances denote that the fermentation is progressing satisfactorily, and it now only becomes necessary to keep it steady and under control, by maintaining the temperature at 45°—50° C., adding, every two or three hours, a portion (one-eighth to one-fourth) of the remaining quantity of lime, and vigorously stirring the whole contents of the vat after each addition. In the course of the next twelve to twenty-four hours, provided the fermentation continues to progress favourably, the vat is ready to be used for dyeing. Excessive fermentation is prevented by well-timed and suitable additions of lime; sluggish fermentation, on the contrary, is accelerated by making further additions of bran. The dyeing power of the vat is maintained by adding, after each day's work, fresh quantities of lime and bran, and every other day 5—8 kilos. Indigo; care being taken to keep the temperature of the liquor at about 50° C. After three or four months, or whenever the vat sediment becomes so bulky that there is a difficulty in obtaining the clear-liquor space necessary for good dyeing, no further additions of Indigo are made; the vat is then used for dyeing light blues, and when its colouring power is exhausted, the whole contents are thrown away. The woad vat gives rich and brilliant colours, and serves equally well for light and dark shades of blue. It is the vat most largely employed in Yorkshire for woollen dyeing.

240. Potash Vat.—This vat is made up with the following ingredients: Indigo, 10 kilos.; Madder, 2—5 kilos.; bran, 2—5 kilos.; carbonate of potash, 10—15 kilos. The bran and Madder are first heated to 80°—100° C. for 3—4 hours with water, after which the potash is added and dissolved, and the liquor is allowed to cool down to about 40° C. The ground Indigo is then added, the whole is well stirred, and left for a period of 48 hours to ferment, only an occasional stirring every 12 hours or so being needed.

The appearances of a healthy state of fermentation in the potash vat are similar to those observed in the woad vat.

This vat, owing to the absence of such a highly nitrogenous substance as woad, is less liable than the woad vat to get out of order, and is altogether more easily managed. It also dyes more rapidly than the woad vat, gives deeper but duller shades of blue, and the colour does not come off so much on milling with soap and weak alkalis. It is best adapted for very dark shades of navy blue. If unspun wool is dyed in this vat, care must be taken to wash it thoroughly in water afterwards, otherwise it is apt to spin badly.

241. Soda Vat (German Vat).—This vat is set with the following materials: 10 kilos. of Indigo, 60—100 kilos. of bran (or 10—15 kilos. of treacle, instead), 20 kilos. of carbonate of soda crystals, 5 kilos. of slaked lime.

The bran is first boiled with the water for 2—3 hours, the liquid is then cooled down to 40°—50° C., the remaining ingredients are added, and the whole is well stirred up and left to ferment for 2—3 days, with only an occasional stirring. During the progress of the fermentation, lime and soda, as occasion requires, are added from time to time. After being used for dyeing, the vat is replenished with Indigo, soda, and lime. This vat is cheaper than the potash vat, because of the difference in price between potash and soda; it also lasts longer. It is, however, more liable to get out of order, though always more easily managed than the woad vat.

242. Urine Vat.—This vat, although of minor importance, is suitable for working on a small scale. It is used by those who only require to dye vat-indigo blues occasionally, or in comparatively small quantities. The vat is made up as follows:—Add to 500 litres of stale urine, 3—4 kilos. of common salt, and heat the mixture to 50°—60° C. for 4—5 hours, with frequent stirring; then add 1 kilo. of Madder and 1 kilo. of ground Indigo, stir well, and allow to ferment till the Indigo is reduced. In this vat the indigo-white dissolves in the ammonium carbonate arising from the decomposition of the urea contained in the urine.

243. Hydrosulphite Vat.—The active reducing agent in this vat is a solution of hyposulphurous (hydrosulphurous) acid, which may be produced by the action of zinc upon a solution of sulphurous acid, according to the following equation:

$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3} + \underset{\text{Zinc.}}{Zn} = \underset{\substack{\text{Hyposulphur-}\\\text{ous acid.}}}{H_2SO_2} + \underset{\text{Zinc oxide.}}{ZnO.}$$

In practice the zinc is allowed to act upon a concentrated solution of sodium hydrogen sulphite (bisulphite), instead of sulphurous acid, in which case the reaction is somewhat more complicated, there being produced a solution of sodium hydrogen hyposulphite and zinc sodium sulphite which separates out, thus:

$$Zn + \underset{\text{Sodium hydrogen sulphite.}}{3NaHSO_3} = \underset{\text{Sodium hydrogen hyposulphite.}}{NaHSO_2} + \underset{\text{Zinc Sodium sulphite.}}{ZnNa_2(SO_3)_2} + H_2O.$$

The reduction of the indigotin by means of the acid sodium hyposulphite may be represented by the following equation:

$$\underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + \underset{\text{Acid sodium hyposulphite.}}{NaHSO_2} + NaHO = \underset{\text{Indigo-white.}}{C_{16}H_{12}N_2O_2} + \underset{\text{Disodium sulphite.}}{Na_2SO_3}.$$

It is not customary to reduce the indigo in each vat separately, but rather to make a very concentrated solution of reduced indigo, and to use this stock solution for preparing and replenishing the dye-vats.

The setting of a hydrosulphite vat naturally divides itself into three phases.

1st, The formation of acid hyposulphite of soda according to the above equation.

2nd, The changing of this acid hyposulphite into neutral hyposulphite by mixing it with lime.

3rd, The mixing of this solution with Indigo and a further quantity of lime, in order to produce the stock solution of reduced indigo. Fig. 84 shows a suitable apparatus in which to conduct the first two operations.

(1) A vessel A provided with an agitator, and which can be hermetically closed, is packed full of small rolls of zinc-foil, then filled up with bisulphite of soda, 55° Tw. (Sp. Gr. 1·275), and thoroughly saturated with sulphurous acid. The size of the vessel should be just adapted to the quantity of hyposulphite required for immediate use, and so that it may be entirely full of zinc, in order to

prevent oxidation as much as possible. The zinc and bisulphite of soda are allowed to act upon each other, with occasional stirring, for about an hour at least. The sodium hydrogen hyposulphite thus produced stands at 62° Tw. (Sp. Gr. 1·31), and, since it is very unstable, it must be used at once, either for reducing indigo or for making the neutral sodium hyposulphite. One litre bisulphite of soda, 55° Tw. (Sp. Gr. 1·275) requires 100—125 grams of zinc, of which quantity about 50 grams dissolve during the operation. Granulated zinc or zinc powder may be used instead of zinc-foil, but the former retains much of the liquid when the vessel is emptied, and cannot be so readily washed. The latter is perhaps the best form of zinc to use, but it varies considerably in composition, and owing to its being in the state of such a fine powder, the liquid heats considerably during the mixing, so that there is always the danger of a portion of the hyposulphite being decomposed. Whenever the acid hyposulphite of soda has been drawn off, the zinc should be rinsed with water, and, if not immediately required again, the vessel should be filled up with water, in order to prevent, as much as possible, the oxidation of the zinc.

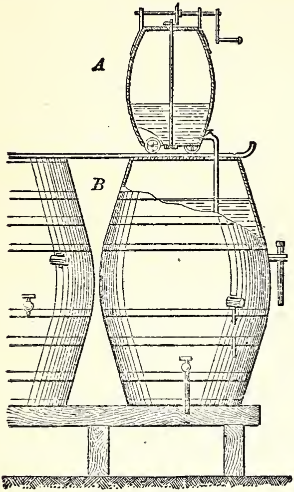


Fig. 84.—Apparatus for Preparing Hydrosulphite Vat Liquor.

When a fresh quantity of hyposulphite is to be made this water is drawn off and the zinc is rinsed, first, with water slightly acidulated with hydrochloric acid, and afterwards with water. The small quantity of zinc dissolved in the previous operation is replaced by an addition of fresh zinc-foil, so that the vessel may be entirely full. Bisulphite of soda solution is then poured over it, and the process as already described is repeated.

(2) In order to change the unstable *acid* sodium hyposulphite thus produced into the more stable *neutral* hyposulphite, it is drawn off into another closed vessel B, and there mixed with milk of lime, which precipitates zinc oxide and calcium sulphite. One litre of acid sodium hyposulphite, 62° Tw. (Sp. Gr. 1·31) requires about 460 grams of milk of lime, containing 200 grams of quicklime per litre. The mixture is well agitated, and after settling the clear liquid is drawn off. A better yield is obtained by passing the mixture through a filter-press. The weight of neutral hyposulphite thus obtained is about the same as that of the original sodium bisulphite, and it has a density of about 36° Tw. (Sp. Gr. 1·12). It is best to employ the solution as soon as possible for reducing Indigo, and not to make more than is required for immediate use. If it is ever found necessary to keep it for some time, it must be made alkaline by adding a little lime.

(3) The stock solution of reduced indigo is made by heating to a temperature of 70°—75° C. the following mixture: 1 kilo. of Indigo, 1—1·3 kilos. of milk of lime (containing 200 grams. of quicklime per litre of water), and so much neutral hyposulphite, 36° Tw. (Sp. Gr. 1·18), as is obtained from 8—10 kilos. of concentrated sodium bisulphite. The indigo is rapidly and completely reduced, and a comparatively clear greenish-yellow solution is obtained, containing about one kilo. of Indigo per 10—15 litres of solution. With an insufficiency of lime, part of the indigo-white is not dissolved, but remains as a dense white precipitate. In setting a hydrosulphite vat, the vat is first filled with water heated to 50° C.; it is then deprived of the oxygen it naturally contains, by adding a little of the neutral hyposulphite. The concentrated stock solution of reduced indigo is then added in sufficient quantity to make a vat of the required strength,

and since there is no sediment, the dyeing may be at once proceeded with. The dyeing power is maintained by adding fresh quantities of the concentrated solution of reduced indigo. The liquid of the vat should always contain an excess of hyposulphite. It should have a yellow colour, and be clear.

If from any cause excessive oxidation of the indigo-white takes place, and the liquor becomes greenish, a little more hyposulphite, and possibly also milk of lime, must be added, and the whole heated to 70°—75° C., in order to accelerate the reduction of the indigo and restore the normal yellow colour. When the vat is in use the alkalinity of the liquid increases, and there is a danger of both the colour and the fibre being injured; hence it is advisable to partially neutralise the excess of alkali from time to time, by making slight additions of dilute hydrochloric acid.

244. Defects in Indigo Vats.—All the fermentation vats are subject to derangements, by which they become more or less useless. The most serious defect is produced by using a deficiency of lime, in which case the fermentation becomes more and more active; if allowed to proceed too far, the indigo is totally and irretrievably destroyed.

This defect is recognised by the following characteristics: The flurry disappears, the vat liquor has a muddy appearance, and gives off a very disagreeable odour; it has a dirty reddish-yellow tint, and acquires the property of gradually destroying the colour of a small piece of indigo-blue cloth, which may be plunged into it.

The only remedy to be applied, in such a case, is to heat the vat liquor to 90° C., and add lime or potash, &c., according to the kind of vat. If this has not the effect of arresting the fermentation, the vat will "run away," or be "lost," as the dyers term it. The woad vat is the one most liable to this defect, because it contains a very large quantity of nitrogenous matter.

Another defect is caused by working the vat too hard, *i.e.*, dyeing too many pieces in rapid succession. Under these circumstances the appearance of the vat becomes very similar to that exhibited in the last defect, but the odour is faintly ammoniacal. A vat in this state gives much paler colours than when it is in its normal condition. To remedy this defect, it is advisable, first, to add a little lime—perchance one might have been deceived by the colour of the vat—and, after some time, to add a little woad and warm the vat, endeavouring thus to promote rapid reduction of the precipitated indigo, and to get rid of the excessive amount of oxygen which has been introduced into the vat. A quicker method is to add a small quantity of ferrous sulphate, and then to stir up the liquor thoroughly.

A third defect is caused by the presence in the vat of such an excess of lime, as to precipitate the indigo-white. In this case, the vat liquor becomes of a dark brown colour, and the healthy odour and the blue scum or "flurry" disappear. When noticed in time, this defect is remedied by adding, at intervals, a small quantity (say half a kilo.) of ferrous sulphate, or of dilute sulphuric acid, and stirring up the vat. This addition precipitates the excess of lime as calcium sulphate.

245. **Dyeing with the Indigo-Vat.**—The operations involved in setting, working, and keeping the fermentation indigo-vats in order, are very simple, but since the phenomena of fermentation are for the most part extremely complex and ill-understood, long-continued and close observation is necessary before one is able at a glance to recognise the features characteristic of the very various conditions which the vat liquid may assume.

Woollen material, of whatever kind, must always be well boiled with water, and then at once passed into tepid water, and squeezed, before it is entered into the indigo-vat. It should never be allowed to lie in irregular heaps after boiling, since this causes unequal dyeing. This wetting-out process not only accelerates the absorption of the vat liquor by the material, but also produces more even dyeing, and prevents the introduction into the vat of a large amount of air, which would oxidise the indigo-white, and cause a precipitate of indigo-blue merely to adhere mechanically and loosely to the surface of the material. Cloth previously milled with soap should be well boiled with water and washed, in order to remove all traces of soap, otherwise "cloudy" or irregular dyeing will result, through the precipitation on the cloth of a lime-soap, which, being of a sticky nature, acts as a resist. Before beginning to dye, the blue scum on the surface of the vat liquor must always be skimmed off, in order to prevent it from producing irregular spots on the material, especially in the case of cloth-dyeing.

Loose wool is gently moved about, by means of poles, in that portion of the vat liquor which is above the trammel-net, care being taken at this stage never to bring it above the surface and thus expose it to the air. Loose wool is best dyed in a vat in which the fermentation is slightly active. When it has been immersed, and worked the length of time necessary to obtain the intensity of colour required (say ten minutes to two hours), it is taken out, placed in strong bags of netted cord, and the excess of liquor is well wrung out. The wool is then thrown into heaps, and remains exposed to the air until the blue colour is fully developed. The dyed wool must now be well washed with water slightly acidulated with sulphuric or hydrochloric acid, in order to remove loosely adhering indigo and all soluble material absorbed from the vat, also to dissolve away any adhering lime carbonate. This treatment prevents the greyish appearance the blue would otherwise acquire on drying, and gives it greater brilliancy. The acid must, of course, be entirely removed by a final washing in water before drying.

In dyeing *woollen yarn*, each hank is worked in the vat separately for a short time, and at once wrung out and thrown on the floor to oxidise. To obtain dark shades the whole process must be repeated several times. The subsequent operations of washing, &c., are the same as in the case of dyeing loose wool.

Woollen cloth, after boiling and cooling as already mentioned, is dyed by moving it about, or "hawking" it, in the vat liquid above the trammel-net, by means of an instrument called a "hawk," *i.e.*, a double hook, one of which is held in each hand by the workman. Care must be taken during the whole operation not to raise the cloth above the surface of the liquid, in order to avoid irregular oxidation, and, consequently, uneven dyeing. The duration of the hawking process may vary from twenty minutes to two hours, according to the dyeing power or strength of the vat, the texture of the cloth, and the depth of colour required. Since the vat solution is not so readily and thoroughly absorbed by thick and closely woven cloth, such material requires longer time than if it were thin and loosely woven. In many well-ordered dye-houses, the moving about of the cloth in the vat liquor is effected by a so-called hawking-machine. This consists essentially of a framework, supporting a pair of squeezing rollers a little below the surface of the vat liquor. The cloth to be dyed is opened out, and the ends are stitched together, so as to form a broad endless band; this is continually drawn through the vat liquor and between the squeezing rollers until the shade required is obtained; the squeezing rollers are provided with close-fitting iron scrapers, which prevent the cloth from wrapping round them, and the framework has guiding pegs to keep the cloth from running to one side. The squeezing rollers are turned either by hand or steam-power. Such machines give much more regular work, and in thick cloth the dye may be made to penetrate more thoroughly to the centre of the fabric, it being possible to regulate at will the pressure of the squeezing rollers.

In order to dye to an exact shade of dark blue, the cloth is worked in a strong vat until a blue a little lighter in shade than that ultimately required is obtained; it is then withdrawn from the vat, and the colour is fully developed by exposure to the air, after which the operations are repeated in a weaker vat till the desired shade is gained. If a light shade of blue is wanted, the cloth is at once worked in a weak vat for the requisite length of time. Cloth dyes best in a vat in which the fermentation is kept very moderate. After dyeing, the cloth must be rinsed in acidulated water, and well washed, as already mentioned in the case of loose wool. In order to remove every trace of loosely adhering indigo, a good milling with soap and fuller's earth is eventually given, so that the finished piece will not soil a white handkerchief when rubbed on its surface. Previous to fulling, it is well to boil the goods with a solution of alum or bichromate of potash and tartaric acid. This operation makes the colour much faster against light and rubbing. As a rule, the loose indigo removed during the fulling operation is allowed to run to waste, but it is probable that much of it might be profitably regained from the sediment of the fulling mills, by a system of washing based on the difference of Specific Gravity between the fuller's earth and indigotin; or one might mix the sediment with ferrous sulphate solution, let settle, draw off the clear solution of reduced indigo, oxidise it, and collect the regenerated and precipitated indigo.

By boiling the cloth (after dyeing and washing) with Barwood, Sanderswood, or Camwood, the blue is said to be better fixed and faster against light than without this treatment. It is not so liable to bleach at the cut edges, &c. Steaming the goods for half an hour makes the blue a little more violet, but faster against light. Vat-blues, which have been boiled with alum and tartar after dyeing, become slightly paler by the operation, but are rendered much more stable against light; the ultimate gain being much greater than the primary loss. Exposure to light gives vat-blue a violet tint. By boiling with alum and tartar, after dyeing and washing, &c., and steaming half an hour in addition, the colour is only slightly weaker, and the greatest fastness against light is obtained. If treated in this way, the colour becomes darker during the first five months of exposure to light and air, and at the end of the year possesses the same depth of shade as at first. From these facts it may be inferred that in the case of woaded browns, greens, &c., the dyeing in the woad-vat should precede the mordanting and dyeing of the added colours.

246. *Application to Silk.*—Silk is now seldom dyed vat-blue. Lime tends to make the silk harsh and brittle, hence it is well to employ the soda or potash vat, the hydrosulphite vat, or, better still, a vat in which the Indigo is reduced by zinc powder and ammonia.

247. **Indigo Extract; Indigo Carmine** [$C_{16}H_8N_2O_2(HSO_3)_2$]. This colouring matter is the product of the action of strong sulphuric acid on Indigo.

248. *Application to Cotton.*—Indigo Extract has no affinity for cotton, and cannot be used by the cotton dyer. It is, however, occasionally used by bleachers for tinting.

249. *Application to Wool.*—The blue obtained on wool, by means of Indigo Extract and Indigo Carmine, is sometimes called "Saxony blue." It is a much brighter colour than that obtained by means of the indigo-vat, but is very far from being so fast either to light or to the action of soap and weak alkalis. Hence it does not stand milling well. Wool must always be dyed with the above-mentioned colouring matters in an acid bath. When "sour extract" (*i.e.*, indigotin-disulphonic acid, containing free sulphuric acid) is used, no other addition to the dye-bath than the Extract itself is necessary. The wool may be entered at 40°—50° C.; the temperature of the bath should then be gradually raised in the course of half an hour to the boiling point, the dyeing continued for half an hour longer. By dyeing at 70°—80° C., a purer blue is obtained, but the colour is apt to have an uneven, speckled appearance. Boiling levels the colour, but makes the shade greener. When Indigo Carmine is employed, this being the sodium

salt of indigotin-disulphonic acid, it is necessary to add to the dye-bath, along with the colouring matter, 5—10 per cent. of sulphuric acid, 168° Tw., so that this may combine with the sodium, and liberate the colour-acid itself. Without this addition the full colouring power of the Indigo Carmine would not be developed. The addition of 10—20 per cent. of sodium sulphate to the dye-bath along with sulphuric acid tends to make the colour uniform or level. Sometimes alum is also added to the bath in order to mordant the wool slightly, and permit the application of Logwood and other polygenetic colouring matters.

250. *Application to Silk.*—Dye at a temperature of 40°—50° C., in a bath acidified with sulphuric acid, and containing the amount of Indigo Carmine solution necessary to produce the depth of shade required.

Another method is, to mordant the silk first with alum by steeping twelve hours in a solution of 25 per cent. of alum, and then, without washing, to dye in a solution of Indigo Carmine with the addition of about 10 per cent. of alum to the dye-bath. If scroop is required, a further addition of a little acetic acid or cream of tartar is necessary.

In this case the alum acts in no sense as a mordant for the Indigo Carmine, but makes it possible to redden the shade, or even to produce a violet colour, by adding Cochineal decoction to the dye-bath; by the further addition of decoctions of Old Fustic, Logwood, Orchil, &c., various shades—grey, drab, brown, &c.—may be obtained, according to the amount of each colouring matter employed.

By adding to the dye-bath a decoction of 10—20 per cent. of Logwood, a dark shade of blue is obtained; the addition of too much Logwood decoction, however, must be avoided, otherwise the colour is apt to become dull. The most rational method of adding the colour yielded by Logwood to that of the Indigo Carmine, is to dye with the two colouring matters in separate baths.

LOGWOOD.

251. This dyewood consists of the heart wood of *Hæmatoxylon campechianum*, growing in Central America.

252. *Application to Cotton.*—The principal use of Logwood in cotton-dyeing is for the production of blacks and greys; it may, however, also serve for purples, blues, and numerous composite colours. In conjunction with other colouring matters, it is employed for the production of numerous compound shades, its use being, in such cases, to make the colour darker, or of a bluer tone.

253. Logwood Blacks.—The method of obtaining a logwood black consists essentially in mordanting the cotton with a salt of iron, and then dyeing with a decoction of Logwood. Numerous modes of applying this simple process are in general use, but the principle is always the same.

In order to mordant the cotton, it may be worked in a cold solution of pyrolignite or nitrate of iron, at about 5° Tw. (Sp. Gr. 1·025) till thoroughly saturated; after squeezing, the iron is fixed by working in a cold weak bath of sodium carbonate, or milk of lime; the cotton is finally well washed in water.

Another method of mordanting, and one which gives faster blacks, is to fix on the fibre a tannate of iron instead of ferric oxide, as in the last case. Work the cotton in a cold infusion of about 30—40 per cent. of Sumach, or its equivalent of other tannin matter (ground Gall-nuts, Myrabolams, &c.), and allow it to steep for several hours, or even over-night; remove the excess, and, without washing, work for about half an hour, in a cold solution of pyrolignite or nitrate of iron at 2°—4° Tw. (Sp. Gr. 1·01—1·02), and wash well. In order to remove all traces of acid, and to fix more completely on the fibre a basic salt of iron, it is advisable before washing to work the cotton in a cold bath of chalk-water, or in weak milk-of-lime. Not unfrequently a lime bath is applied immediately after sumaching and before passing into the iron bath. In this case a tannate of lime will be formed upon the fibre, and the double decomposition with the iron salt is facilitated, since the lime at once takes up the acid liberated.

In warp dyeing the whole process is continuous, and the cotton, after being steeped in a decoction of myrabolams is passed successively through baths containing lime-water, nitrate of iron, logwood liquor, dilute iron solution, and water.

For low-class goods, many dyers substitute ferrous sulphate for the pyrolignite and nitrate of iron.

The pyrolignite of iron may also be mixed with an equal or somewhat smaller amount of aluminium acetate (red liquor) at 5° Tw. (Sp. Gr. 1·025), in which case it may be better to fix the mordants by working the cotton for a quarter of an hour at 50°—60° C., in a dilute solution of phosphate or arsenate of soda.

An aluminium mordant alone would give a dull lilac shade, but along with an iron mordant it helps to remove the unpleasant reddish or rusty appearance of the blacks otherwise obtained.

When Catechu is the tannin matter employed, the cotton should be worked in a *boiling* decoction of it, and allowed to steep till cold, in order to effect the precipitation on the fibre of the maximum amount of catechin. The cotton may afterwards be worked 5—15 minutes in a boiling solution of bichromate of potash (five grams per litre), before passing it into the bath of pyrolignite of iron, though this is not absolutely necessary.

By whichever method the mordanting is effected, the dyeing takes place in a separate bath containing a suitable amount of freshly-made Logwood decoction, together with a small quantity of extract of Old Fustic, or of Quercitron Bark. If an iron mordant only has been employed, it is beneficial to add also a small quantity of copper sulphate to the dye-bath, in order to prevent the cotton from acquiring the rusty appearance already referred to.

The cotton is introduced into the cold dye liquor, and the temperature is gradually raised to the boiling point.

After dyeing, the cotton may be passed through a solution of bichromate of potash, 0.5 grams per litre, at 60° C. This operation gives intensity and fastness to the black, since any excess of colouring matter is fixed as a chromic oxide lake.

The dyed cotton is washed and worked in a solution of soap, five grams per litre, at a moderate temperature, then squeezed and dried. This final soaping removes any bronze appearance, and imparts to the colour a bluer and more agreeable tone. The cotton also acquires a softer feel.

The following is a method by which a chrome black on cotton can be obtained in a single bath:

Dissolve 1·5 kilos. of bichromate of potash in a small quantity of water, mix the solution with 500 litres of Logwood decoction at 3° Tw. (Sp. Gr. 1·015), and add 3·5 kilos. of hydrochloric acid, 34° Tw. (Sp. Gr. 1·17). The cotton is introduced into the cold solution, and the temperature is very gradually raised to the boiling point. The cotton acquires at first a deep indigo-blue shade, which changes to a blue-black on washing with a calcareous water.

A slight modification of this process which may be adopted, is to work the cotton in a solution containing at first only the bichromate of potash and hydrochloric acid, and to add the decoction of Logwood to the bath, in small portions from time to time, gradually raising the temperature as before.

Another method of producing a Logwood black, is to dye in a bath containing Logwood extract, and copper acetate, entering the cotton cold, raising the temperature gradually to 50° C., and dyeing at that temperature until the colour is sufficiently developed.

Copper sulphate, to the amount of about 4 per cent. of the weight of cotton, is frequently used instead of acetate, and an addition of 4 per cent. of soda-ash is made to the bath along with 20 per cent. of solid Logwood, extract.

The cotton is passed rapidly through this mixture, heated to 60°—80° C., and then allowed to oxidise or "smother" for 5—6 hours. This process requires to be repeated several times before a full black is obtained. The method is not economical for ordinary use, but it is said to yield a black which withstands milling with soap very well. Carbonate of copper may also be applied in the above process, instead of copper sulphate and soda-ash.

The methods already given may be adapted to the dyeing of unspun cotton. The following method of dyeing a chrome black is said to be specially applicable to such as must withstand the operation of fulling. Wet out the cotton well in boiling water, then boil in a strong solution of about 30 per cent. of solid Logwood-extract, drain, and allow it to lie exposed to the air for some time; complete the oxidation thus begun, by working it one hour in a cold solution of 8 per cent. of bichromate of potash and 6 per cent. of copper sulphate, wash and complete the dyeing in a bath containing 10 per cent. of Logwood extract; enter the cotton cold, and raise the temperature gradually to the boiling point. Wash, soap, and dry.

In the first bath the cotton simply absorbs the colouring matter of the Logwood; in the second this is oxidised, and at the same time combined with a sufficient amount of mordant, copper and chromic oxide, to enable it to take up still more colouring matter in the third bath. The first Logwood bath is analogous to the tannin bath alluded tc in a previous process (p. 319).

254. **Logwood Greys** are obtained by working the cotton for a short time at 40°—50° C. in a weak decoction of Logwood (1—5 per cent.), then in a separate bath containing a weak solution of ferrous sulphate or potassium dichromate, and washing. Many dyers adopt the apparently irrational method of mixing the ferrous sulphate and Logwood solutions, and dye at once in the inky liquid thus obtained. Comparatively little precipitate,

however, is produced in the dye-bath in this case, and the colour is for the most part developed on the cloth itself during the subsequent oxidation by exposure and washing. The shade of grey may be modified *ad libitum*, by adding to the Logwood bath a small proportion of decoctions or extracts of tannin matter, Old Fustic, Peachwood, &c.

255. **Logwood Purples** are obtained by mordanting the cotton in a weak solution of stannous chloride, then washing and dyeing in a separate Logwood bath. The colour is tolerably fast to soap, but not to light.

256. **Logwood Blues** on cotton are now seldom dyed, because of their fugitive character. To obtain them, work the cotton in a bath containing a decoction of Logwood and a small proportion of copper acetate or sulphate, raising the temperature gradually to 50° C. The tone of colour has great similarity with that of an indigo-vat blue.

257. *Application to Wool.*—Logwood is the essential basis of all good blacks on wool, although other colouring matters are frequently used along with it, either to modify the particular shade of black, or to add to its intensity and permanence.

According to the materials employed, we may distinguish the following kinds, *Chrome black*, *copperas black*, and *woaded black.*

258. **Chrome Blacks** are produced by first mordanting the wool for 1—1½ hour at 100° C., with 3 per cent. of bichromate of potash and 1 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), then washing and dyeing in a separate bath for 1—1½ hour at 100° C., with 35—50 per cent. of Logwood. This represents the simplest form of dyeing a chrome black, but in practice numerous slight modifications are introduced, in order to obtain various shades of black. The following, which are typical, may be mentioned. The mode just given yields a *blue-black*, or, as it is sometimes called, a black with blue reflection. By the addition of a suitable amount of some yellow colouring matter to the dye-bath—*e.g.*, 5 per cent. Old Fustic—a

dead-black is obtained, *i.e.*, a neutral black, which possesses no decided tint of blue, green, violet, &c. By increasing the amount of Old Fustic to 10 per cent., a *green-black* is obtained, and the greenish shade becomes still more pronounced, if 3—4 per cent. of alum is added to the mordanting bath along with the bichromate of potash.

A *violet-black* is produced by dyeing exactly as for blue black, but after the dye-bath has been exhausted, a dilute solution of about 2 per cent. of stannous chloride (tin crystals), or its equivalent of commercial muriate of tin containing no free acid, is added to the dye-bath, and the boiling is continued 15—20 minutes longer.

In the case of dead-blacks, it is the custom with some dyers to "sadden" in a similar way with 3—4 per cent. of ferrous sulphate; or instead of this, the goods are passed, after dyeing, through a warm bath containing about 0·5 per cent. of bichromate of potash. The object of these last modifications is to precipitate and fix more completely on the wool any colouring matter, perchance not combined with the mordant, but simply absorbed by the wool.

With black yarn, which will eventually appear in a woven fabric, in close proximity to white or delicately-coloured yarns, this fixing of the dye is very necessary, otherwise the light-coloured or white yarns become stained during the operations of milling, &c., and the finished fabric has a soiled appearance. It is always the case that some black comes off during these operations, but if the colouring matter of the Logwood is thoroughly combined with its own mordant, it will not readily combine with the mordant of any neighbouring fibre, but be simply rubbed or washed out as an insoluble powder.

Chrome blacks may also be dyed in a single bath, as follows : A mixture of Logwood liquor and bichromate of potash solution in suitable proportions is boiled. The precipitate thus produced is collected, and may then be employed as a "direct black," or a "one-dip dye." It is, indeed, the actual coloured body or pigment one wishes to fix upon the wool, and this is rendered possible, because not only is the precipitate soluble in an acid solution, but the wool is capable of attracting it from the solution. The precipitate is added to the dye-bath, along with just sufficient oxalic acid to dissolve it, and the wool is dyed in the solution at 100° C., for one and a half hour. Good results are, however, not so readily obtained as when iron and copper mordants are used (*see* Bonsor's black, p. 329).

259. Indigo Substitute.—This product, at present sold in the form of a purplish-blue liquid, is said to be produced by boiling together Logwood extract and chromium acetate. Cotton is dyed by simply working it in a hot solution of the mixture.

Of all the blacks derived from Logwood, the chrome black is the one least affected by acids. If tested by spotting with strong sulphuric acid, it becomes a dark olive colour. It also resists the action of scouring and fulling very well. On the other hand, however, chrome blacks are not altogether satisfactory as regards their behaviour on exposure to light. They gradually assume a greenish hue, although otherwise they are tolerably fast.

The greening of a chrome black is most apparent when Logwood, or Logwood and Old Fustic, have been employed in dyeing. Its bad effect may be counteracted by the addition of a suitable red colouring matter to the dye-bath—*e.g.* Alizarin—or by dyeing the wool a reddish-brown colour before dyeing with Logwood. This is very conveniently carried out in practice by boiling the wool with 6—8 per cent. of Camwood for an hour, then adding to the exhausted bath the bichromate of potash (generally with the addition of a small percentage of alum and tartar), and mordanting, &c., as already given.

Owing to the comparatively small proportion of bichromate of potash required to produce the fullest blacks, there is evidently a minimum quantity of lake precipitated on the fibre, so that the latter retains very much its pristine elasticity and softness.

Excess of bichromate of potash should always be avoided, since the colour is then more liable to become green, or to fade, on exposure to light.

260. The use of Bichromate of Potash.—The following results of experiments on the use of chromium mordants will be of interest.

By mordanting the wool with 3 per cent. of bichromate of potash, a full and bright shade is obtained. The use of more than this amount causes the colour to become dull and grey (over-chroming, *see* p. 209).

The employment of sulphuric acid along with the bichromate of potash is advantageous when the proportion does not exceed one molecule of sulphuric acid to one molecule of bichromate of potash, *i.e.*, 1 per cent. of sulphuric acid 168° Tw. to 3 per cent. of bichromate of potash.

When used in this proportion it gives a brighter and somewhat deeper shade than can be obtained from bichromate alone; but should the above-mentioned amount be exceeded, a dull grey appearance results, which becomes more apparent as the amount of sulphuric acid increases.

If the bichromate of potash be increased along with the sulphuric acid, the injurious effects of "over-chroming" are intensified.

The addition of tartar or tartaric acid to the mordanting bath, along with bichromate of potash, is beneficial, the shades being much more brilliant, though somewhat lighter, than when sulphuric acid is used.

Tartaric acid gives decidedly brighter and more purple shades than tartar. The best results are obtained by using 6 per cent. of tartaric acid or 8 per cent. of tartar to 3 per cent. of bichromate of potash.

Oxalic acid is also beneficial in the mordanting bath, and in this case, 4 per cent. of oxalic acid to 3 per cent. of bichromate of potash yields the best results.

On comparing the shades obtained by using these acids in the mordanting bath, it is seen that they are all better than can be obtained by bichromate of potash alone.

The addition of sulphuric acid produces a deep, dead-looking blue-black; tartar or tartaric acid yields a bright bloomy bluish-black; oxalic acid a black which is darker, duller, and slightly greener than can be obtained with tartar or tartaric acid, but not so dark as with sulphuric acid.

Whenever bichromate of potash alone is employed, the mordanted cloth has a dull yellow colour, but if tartar or tartaric acid has been added to the bath, it is a pale bluish-green.

From these results it would appear that the best shade is obtained when the chromium mordant is fixed on the cloth in the state of chromic oxide previous to the application of the Logwood.

The substitution of chrome alum as a mordant in place of bichromate of potash does not give good results, the ultimate colour obtained having an irregular speckled appearance, evidently owing to the unequal deposition of the chromic oxide; besides a very large proportion of tartar must be used to obtain a full shade.

When the cloth has been mordanted with bichromate of potash alone, or with bichromate of potash and sulphuric acid, the presence of chalk or calcium acetate in the dye-bath is decidedly injurious. The acetate seems to be least hurtful, although, even with this, the addition of more than 2 per cent. gives the colour a greyish appearance. If tartar has been employed along with the bichromate of potash, the presence of calcium acetate is decidedly beneficial, the shade being intensified from a pale blue when no calcium acetate is used, to a deep indigo-blue when 30 per cent. is employed. The best amount to use appears to be 30 per cent., but even 80 per cent. may be added to the dye-bath without any great detriment, the colour merely losing a little brilliancy and purple tone, and becoming blacker.

261. **Copperas or Ferrous Sulphate Black.**—This black was formerly the one in general use, but since the introduction of the chrome black, it has been more or less discontinued. It is often used for low-class carpet, yarns, &c.

Two methods may be employed, namely, that of mordanting the wool first and dyeing afterwards, or that in which the wool is first boiled with Logwood and afterwards saddened.

It is usual to add along with the ferrous sulphate a small proportion of copper sulphate, and when the first method is employed, argol, and frequently also alum, is added.

Example of first method. — Mordant the wool for 1½—2 hours with 4—6 per cent. of ferrous sulphate, 2 per cent. of copper sulphate, 2 per cent. of alum, 8—12 per cent. of argol; take out, squeeze, and let lie overnight. Dye for 1½ hour with 40—50 per cent. of Logwood.

Example of second method.—Boil the wool for one hour with a decoction of 40—50 per cent. of Logwood, and 5—10 per cent. of Old Fustic; lift, cool the bath, add 4—6 per cent. of ferrous sulphate, and 2 per cent. of copper sulphate, re-enter the wool, raise the temperature to 100° C. in three-quarters of an hour, and boil half an hour. The first method is the more economical.

The amount of tartar or argol used along with the ferrous sulphate in the first method has considerable influence on the beauty of the colour; with too little it is grey and dull; an excess is less hurtful. Experiment shows that the relative proportions should be—1 molecule of ferrous sulphate, 2—3 molecules of cream of tartar. There is no advantage in using more than 6 per cent. of ferrous sulphate. Wool mordanted with ferrous sulphate alone is buff-coloured from deposition of ferric oxide; when tartar is used its colour remains almost unchanged. If the water employed is not calcareous, the addition of 3 per cent. of chalk, or preferably calcium acetate, to the dye-bath increases the intensity of the colour. The use of a lime salt here does not appear to be so effective as with chromium or aluminium mordants. As with the chrome black, so here the addition of a yellow colouring matter to the dye-bath is necessary in order to obtain a dead-black; without such addition a ferrous sulphate black possesses a bluish-violet hue. The addition of relatively small proportions of Madder, Sumach, &c., aids in giving a fuller and faster black. Sumach, or other tannin matter, when used alone, is incapable of giving a black on wool with ferrous sulphate.

When dyeing unspun wool or yarn it is preferable to use a freshly-made decoction of Logwood, or a good commercial Logwood Extract, in order to keep the material clean and free from ground dyewood, since this would interfere in the carding.

The ferrous sulphate blacks become red if spotted with strong mineral acid, and are thus readily distinguished from chrome blacks. They bear the action of scouring and milling satisfactorily, and withstand the action of light better than the chrome blacks. Experiment proves that with regard to fastness against light a simple copper sulphate black is the best, so that the use of copper sulphate along with the ferrous sulphate or potassium dichromate is distinctly beneficial. The use of alum is, on the contrary, detrimental in this respect. The copper sulphate will probably also aid in developing a fuller black by reason of its oxidising action upon the hæmatoxylin.

When employed alone, copper sulphate gives greenish shades of blue, having a slightly speckled appearance. The best proportions to employ appear to be 5 per cent. of copper sulphate, and 5·5 per cent. of tartar. An excess of tartar causes the shade to become much lighter. With these amounts, and varying the quantity of Logwood, a series of shades, ranging from pale blue to black, may be obtained, but the lighter shades have a distinct greenish appearance when examined overhand not observable in the darker shades.

The mordanting and dyeing method yields the deepest and most useful shades. The addition of lime salts to the dye-bath is only slightly beneficial.

262. **Bonsor's Black.**—This "direct black," originated by P. Watinne-Delespierre of Lille, consists of a black

paste, produced by precipitating a decoction of Logwood with a mixture of ferrous and copper sulphate. It is applied in the same way as the direct chrome black already referred to.

Add to the dye-bath 25—30 per cent. of the black paste, and about 2—3 per cent. of oxalic acid. The wool is dyed at 100° C. for 1—2 hours.

It is essential that the solution should not be too acid, or it will not yield its full colouring power. The normal colour of the solution is dark-brown; if blue or green in tint, it is a sign of the presence of undissolved precipitate, and a further slight addition of acid must be made.

As the dyeing proceeds, the solution necessarily becomes more and more acid, and it is well before taking out the wool to add a small quantity of sodium carbonate, to neutralise the excess.

If a deeper shade is wanted, one may add along with the black paste some extract or decoction of Logwood. For a jet-black or dead-black some suitable yellow colouring matter may be added in small quantity, *e.g.*, Old Fustic Extract, &c. Such additions, however, alter the normal colour of the solution, and a little experience in their use is required.

The spent dye liquor should be kept, and may serve again if replenished with further quantities of black paste and oxalic acid.

It is possible to use this black along with other so-called acid-colours for the purpose of obtaining composite colours, *e.g.*, in the dyeing of unions.

263. **Woaded Blacks** are obtained by first dyeing the wool in the indigo-vat to a light or medium shade of blue, then washing well, and dyeing as for chrome or ferrous sulphate blacks. If the chrome-black method is selected, it is advisable to make the addition of tartaric acid to the mordanting bath, in order to reduce to a minimum the oxidising action of the bichromate of potash, and the consequent deterioration of the indigo blue.

264. Logwood Blues (Wool).—These are much employed by dyers, in order to imitate an indigo-vat blue. They are often combined with the latter by first dyeing the wool a comparatively light blue · in the indigo-vat, and then intensifying it by one or other of the methods now to be described.

Logwood blues are best dyed in two baths, the mordants employed varying in composition and in amount according to the particular tint of blue which it is desired to obtain.

One method is as follows: mordant the wool for 1—1½ hours at 100° C. with 4 per cent. of aluminium sulphate, 4—5 per cent. of cream of tartar; wash well, and dye in a separate bath for 1—1½ hour, at 100° C., with 15—30 per cent. of Logwood, and 2—3 per cent. of chalk.

By increasing the amount of alum and tartar the shade is made redder. The addition of the chalk, or preferably calcium acetate, to the dye-bath is very beneficial if the water employed is not calcareous, since it tends to make the colour level, and gives richness and considerable intensity to the blue. When calcium acetate is employed, the best result is obtained by using 30 per cent. of the weight of wool. Some dyers imagine that the use of lime salts in dyeing has only a temporary effect, but this is entirely a mistake; indeed, if distilled water and Logwood liquor be employed, the addition of calcium acetate to the dye-bath becomes just as absolute a necessity for the production of a good full colour as it is for alizarin-red. The colour produced with aluminium mordants is not fast to acids or to light. This difference in respect of fastness to light with the different mordants is somewhat remarkable. A somewhat faster colour is obtained by using along with the alum and tartar 0·5—3 per cent. of bichromate of potash; or, better still, one may mordant entirely with 3 per cent. of bichromate of potash and 1 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). If it is desired to imitate the purplish tint of a vat indigo blue, one may then add to the dye-bath, along with the Logwood, a small proportion of Gallein, Alizarin, Gallocyanin, &c. Another method of imparting this purplish "bloom" is to add 0·5—1 per cent. of tin crystals ($SnCl_2 \cdot 2H_2O$) at the end of the dyeing operation.

The brightest Logwood blues are obtained by dyeing at a temperature somewhat below the boil (90° C.). Prolonged boiling tends to dull the colour.

265. **Logwood Purples (Wool).**—These are now seldom used. They may be obtained by mordanting the wool with 6 per cent. of tin crystals ($SnCl_2 \cdot 2H_2O$), or its equivalent of muriate of tin, with the addition of 9 per cent. of cream of tartar, and dyeing in a separate bath, with 30 per cent. of Logwood. The addition of chalk or calcium acetate to the dye-bath in this case is injurious, since it makes the colour greyer and less intense.

266. *Application to Silk.*—The black dyeing of silk has increased to such an enormous extent, that some, and even very large, establishments are exclusively devoted to it. Judged from the technical standpoint, it must be admitted that this branch has reached a high standard of excellence, although, on the other hand, it is to be regretted that the practice of weighting silk, which, in the case of black, may reach as high as 400 per cent., has been so much developed. From 100 kilos. of raw-silk the dyer produces 500 kilos. of black silk! The primary object is to increase the volume of the silk fibre, which swells up very considerably, losing, of course, its strength proportionally. The other valuable properties of silk are also more or less deteriorated, and the illusory gain of the buyer is that he requires to pay less for one and the same surface of silk material. This is not the place to combat the arguments brought forward by the manufacturer in favour of weighting silk, but it may be fairly maintained that the advantages gained are bought too dearly, and the durability of weighted silk is certainly too much diminished.

The production of black on silk consists in alternating treatments with iron mordant and tannin matters, with or without a Prussian Blue basis.

According to Messrs. Gillet and Son, the present methods of dyeing black silk may be classified as follows:—

A. Black on boiled-off Silk, 5—15 per cent. loss.

I.—*Black for Hat Plush.*

1. Mordant in cold nitrate-acetate of iron, and wash.

2. Dye in a decoction of Logwood and a sufficiency of Old Fustic Extract. As a rule, 1—2 per cent. of copper acetate, and 5—10 per cent. of ferrous sulphate, are added to this bath.

3. Dye again in a decoction of Logwood and soap.

4. Brighten in a bath containing a little oil.

II.—*Masson's Black for Hat Trimmings.*—These are exclusively Parisian goods, and of limited use. The silk is boiled-off in soap containing Logwood decoction, by which means it is rendered less liable to felt. It is mordanted in a solution of partially oxidised ferrous sulphate, with addition of a little copper acetate, and afterwards dyed with Logwood and soap.

III.—*English Black.*—Formerly in great demand, this black is now of minor importance.

1. Mordant with basic ferric sulphate, and, after allowing the silk to lie for some time, wash well and soap at 85°—90° C.

2. Dye with 50 per cent. of Old Fustic, 10 per cent. of ferrous sulphate, and 2 per cent. of copper acetate.

3. Dye with Logwood and soap.

4. Brighten

IV.—*Black for Velvets.*—The same method as for English black is used, but dye a lighter-coloured black. The tone of colour is frequently modified by giving the silk previously a dark ground of aniline violet or blue. Great care is required in order not to strip off the aniline blue.

B. BLACK ON BOILED-OFF SILK, original weight or weighted 10 per cent.

V.—*Lyons Black* (dating from 1860), for expensive articles.

1. Mordant in a cold strong bath of basic ferric sulphate, 50° Tw. (Sp. Gr. 1·25), once only, and wash.
2. Soap at 85°—90° C.
3. Dye blue with 15—20 per cent. of potassium ferrocyanide and an equal weight of hydrochloric acid. 30° Tw. (Sp. Gr. 1·15). Add the hydrochloric acid in two separate portions.
4. Mordant with basic ferric sulphate, and wash.
5. Give a Catechu bath, 50—100 per cent. at 60°—80° C.
6. Mordant in a cold solution of alum or aluminium sulphate, and wash. The object of using aluminium mordant is to impart ultimately to the silk a violet or blue-black shade.
7. Dye with Logwood and soap. If the shade is too violet, a little Old Fustic is added.
8. Brighten.

VI.—*Mineral Black* (dating from 1840).—This is a light black, not so fine as the last, and is used for "linings." Mordant with basic ferric acetate, and wash; dye Prussian Blue; repeat the mordanting with iron. Prepare with Catechu (100 per cent.) at 80° C. Dye with Logwood and soap. Brighten.

C. BLACK ON BOILED-OFF SILK, weighted 20—100 per cent. (heavy black).

VII.—This black is dyed on organzine and tram for satins, sarcenets, taffetas, &c.

1. Mordant with basic ferric sulphate, then soap. Repeat these operations 1—8 times, according to the amount of weighting necessary.
2. Dye blue; the proportions of potassium ferro-

cyanide and hydrochloric acid vary according to the amount of ferric oxide fixed on the silk.

3. Give a Catechu bath (100—150 per cent.), with the addition of 10—15 per cent. stannous chloride, at 60°—80° C.

The employment of stannous chloride in *weighted* black-silk dyeing has been of the greatest importance, since it facilitates the fixing of the Catechu to a surprising degree, through the formation of a tannate of tin.

4. Give a second bath of Catechu (100—200 per cent.). This is fixed on the silk only by the action of the tin mordant present.

5. Mordant with pyrolignite of iron.

6. Dye with Logwood and soap.

7. Brighten.

Blue shades of black are obtained by repeating operations 5, 4, 6, in the order given, four times. The only factors which affect the limitation of weighting are the strength, elasticity, and lustre of the silk itself. As a rule, boiled-off organzine is weighted to 60—70 per cent., and boiled-off tram to 100 per cent.

D. HEAVY BLACK, weighted to 400 per cent.

VIII.—This is used for fringes and the fancy articles of Paris and Lyons; also for the tram silk for satin, cheap ribbons, &c.

The raw-silk is dyed by working it alternately in chestnut extract and pyrolignite of iron. By repeating these operations fifteen times, the silk is weighted to about 400 per cent. The final processes consist of brightening operations with 10—20 per cent. of olive-oil. In the first chestnut extract bath, tram is soupled by raising the temperature of the bath sufficiently to soften the silk-glue. Different qualities of silk require slightly different treatment. Bengal silk souples easily; Chinese silk less readily than European silk.

E. Fine Black Souples.

IX.—The finest souples are always obtained by using water as soft as possible, like that of the Gier at Saint-Chamond.

1. Mordant with basic ferric sulphate.
2. Give a soda bath at 30°—40° C. Use 50 per cent. of carbonate of soda crystals.
3. Dye blue with potassium ferrocyanide.
4. Souple by working in a bath of gall-nuts, dividivi, or other similar tannin matter. Heat the bath to 90°—95° C., for 1—3 hours, according to the kind of silk. Experience alone enables the workman to judge when the softening or soupling is sufficient.
5. Leave the silk in No. 4 bath until cold, and then add 5—15 per cent. of stannous chloride crystals.
6. Give a soap bath at 30°—35° C., with 60—80 per cent. of soap.
7. Brighten with 5—15 per cent. of oil.

A single iron bath gives 40—50 per cent. of weighting (light souple); two baths give 60—70 per cent.; three give 80 per cent.; four give 80—100 per cent.

F. Black on Raw-Silk.

X.—This is seldom dyed. In order to retain the stiffness of the silk, the silk-glue is not softened, the number of operations is as limited as possible, and the various baths are used at a low temperature. The process consists of working the silk in baths of ferric salt, then in decoctions of Logwood, and Old Fustic.

The mode of fixing iron mordants on silk has been already explained (*see* p. 184).

For boiled-off silk the potassium ferrocyanide baths are employed at a temperature of 55°—60° C., because the formation of Prussian Blue would otherwise proceed only very slowly, creeping, as it were, from the periphery to the centre of the fibre. For souple silks, however, it is necessary to use cold baths. Only a portion of the requisite hydrochloric acid is at first added, in order to avoid dissolving off any basic ferric sulphate.

The relative proportions of Logwood decoction and soap employed, vary according to the black which it is desired to obtain. The usual quantities may be taken as 50 per cent. of soap and 100 per cent. of Logwood; the mixture is employed as a rule only for boiled-off silk. The temperature of the dye-bath varies from 50°—90° C.

The operation of brightening is intended to restore the soft feel and lustre, which have been greatly destroyed by reason of the large amount of foreign matter with which the silk has become encrusted. For boiled-off silk there is used about 1—2 per cent. of olive oil; for souples 5—15 per cent.; and for fringes, &c., 5—20 per cent. The oil is made into an emulsion with carbonate of soda at 60°—70° C., or with caustic potash or soda in the cold, and then immediately mixed in the bath with water. The silk must be worked in the mixture at once, *i.e.*, before any separation of the oil can take place. Very often an addition is made of 40—60 per cent. of citric, tartaric, or acetic acid; seldom hydrochloric acid. The bath should taste slightly sour.

After each mordanting or dyeing operation, the general rule is to wash thoroughly, and then to remove the excess of water in a hydro-extractor, in order not to dilute the succeeding baths.

The usual duration of each operation varies from one to two hours, but in the tannin baths the silk should remain longer; it is frequently left steeping in them over-night.

The *black dyeing of Tussur silk* is a difficulty not yet completely overcome. The shades are not satisfactory, and the fibre becomes covered with metallic-looking spots. Tussur silk is not readily weighted, and does not absorb the iron mordants well. According to Moyret, the following process gives good results:—

1. Boil-off with dilute caustic soda.

2. Mordant once or twice in basic ferric sulphate, and fix by means of a bath of weak caustic soda.

3. Dye with potassium ferrocyanide.

4. Prepare with a weak chestnut extract bath.

5. Mordant with pyrolignite of iron, and repeat operations 4 and 5.

6. Brighten with 6—8 per cent. olive-oil.

CHAPTER XIV.

RED COLOURING MATTERS.

BRAZILWOOD, PEACHWOOD, LIMAWOOD.

267. These dyewoods are obtained from various species of *Cæsalpinia.* Their dyeing properties are similar, and owing to the fugitive character of the colours they yield, they are now employed in dyeing, only to a comparatively limited extent, chiefly for the purpose of modifying the shade of colours mainly derived from other sources.

268. *Application to Cotton.*—With aluminium mordants comparatively dull bluish-red colours are obtained. Work the cotton in a decoction of tannin matter, then in a cold solution of more or less basic aluminium sulphate. Wash and dye in a fresh bath at a low temperature, with a decoction of the dyewood.

The stannic mordants yield brighter and more orange-toned reds. Scarlet may be obtained by mordanting with aluminium and stannic salts, and dyeing afterwards with the addition of some yellow colouring matter to the dye-bath, *e.g.*, Old Fustic.

With iron mordants these dyewoods give violet-grey colours. By using a mixture of aluminium and iron mordants, and by adding a small proportion of Logwood to the dye-bath, dark purple or "plum" colours are obtained.

The colours are not fast to soap. The fastest are those in which the mordant is fixed by the aid of tannic acid.

239. *Application to Wool.*—In wool dyeing these dyewoods are generally employed along with other dyewoods, for producing brown colours, which cannot, however, be regarded as fast or permanent.

The most useful mordant for wool is *bichromate of potash.* By mordanting with 3 per cent. of bichromate of potash, then washing, and dyeing in a separate bath, with small amounts of dyewood, a purplish slate colour is obtained; with large amounts a claret-brown is produced. The addition of sulphuric or tartaric acid to the mordanting bath is not beneficial; it makes the colour redder. The addition of 3—5 per cent. chalk or calcium acetate to the dye-bath makes the shade bluer.

A bluish-red colour is obtained by mordanting the wool with 6 per cent. of *aluminium sulphate* and 5 per cent. of cream of tartar, then washing, and dyeing in a separate bath for ½—1 hour at 80°—100° C. with 40—60 per cent. of dyewood. Still bluer shades are produced by adding to the dye-bath towards the end of the dyeing operation a little ammonia. The addition of 2—6 per cent. chalk or 6—12 per cent. calcium acetate to the dye-bath is very beneficial; it makes the shade bluer and more intense. Brighter shades of red are obtained by adding to the mordanting bath 1 per cent. of stannous chloride, and a small percentage of some yellow colouring matter, *e.g.*, Old Fustic, Flavin, &c. The addition to the dye-bath of skimmed milk or a solution of gelatin in moderate quantity is beneficial; it combines with and renders insoluble and inert the tannin matters present in the wood, thus enabling one to obtain somewhat brighter shades. The single bath method gives fairly satisfactory results, the colour being paler, but more brilliant than by the mordanting and dyeing method. Use 4 per cent. of aluminium sulphate, with addition of 2 per cent. potassium oxalate.

Although the employment of *stannous chloride* as the mordant yields bright reds when it is used in small proportion (say 2—4 per cent. of stannous chloride with 4 per cent. of tartar), it requires the addition of too much tartar (30—40 per cent.) to give a really good colour. *Stannic chloride* also gives bright reds, but here, too, the amount of tartar required is abnormally large—use, say, stannic chloride equivalent to 4 per cent. $SnCl_2 \cdot 2H_2O$ and 32 per cent. of tartar. With tin mordants the addition of lime salts to the dye-bath is injurious.

Copper sulphate as the mordant gives drab or claret-brown shades, according to the amount of colouring matter employed. Use 4 per cent. of copper sulphate. The addition of tartar is not beneficial. The addition of calcium acetate or chalk to the dye-bath is beneficial.

Ferrous sulphate as the mordant gives dark slate and claret. Use 2—5 per cent. ferrous sulphate, and 4—8 per cent. tartar. The addition to the dye-bath of 8 per cent. or more calcium acetate or chalk is essential

270. *Application to Silk.*—These dyewoods are now no longer used by the silk-dyer, having been entirely displaced by the coal-tar colours.

They were formerly used for obtaining crimson shades.

The ordinary method was to mordant the silk with alum, and dye in a separate bath at a low temperature in a decoction of Peachwood, with the addition of a little soap.

Somewhat brighter and faster shades were obtained by working the silk afterwards in a bath containing nitro-muriate of tin, and finally washing.

Bright crimsons were also obtained by mordanting the silk with stannous chloride and tartar, and dyeing afterwards with a decoction of Peachwood.

CAMWOOD, BARWOOD, SANDERSWOOD.

271. These dyewoods are obtained from certain species of *Pterocarpus* and *Baphia;* but although the origin of each is distinct, and the colours they yield vary some-

what in tone, their general dyeing properties are so similar that it will be most convenient to consider their application in dyeing, together.

They are principally used in wool-dyeing, in conjunction with other dyewoods—*e.g.*, Logwood, Old Fustic, &c. —for the purpose of obtaining various shades of brown, olive, drab, &c. In cotton-dyeing their use is more limited, while in silk-dyeing, owing to the great insolubility of their colouring principles and the essential exclusion of all ground wood from the dye-bath, they are not used at all.

272. *Application to Cotton.*—The colours produced on cotton are moderately fast to soap and weak acids, but not to light. They are destroyed by hypochlorites, and boiling alkaline solutions rapidly impoverish them.

With aluminium and tin mordants (especially the latter) fairly good reds can be obtained. These are rendered bluer by the action of soap and alkalis. With iron mordants they yield dull violet colours.

Barwood is chiefly used by the cotton-dyer for the purpose of obtaining "Barwood red," sometimes called "mock Turkey-red."

The cotton is worked in a cold solution of stannate of soda, 4°—6° Tw., till thoroughly saturated, wrung out, and then worked rapidly and for a short time in dilute sulphuric acid, $\frac{1}{2}$° Tw. Wash well, and dye with about 200 per cent. of Barwood. The cotton is introduced into the dye-bath cold, the temperature is then gradually raised to 100° C., which is maintained for an hour or more. By adding a small quantity of sodium carbonate to the dye-bath (about 6 per cent. of the weight of Barwood) the colouring matter is somewhat more readily extracted, and a fuller but slightly duller red is obtained.

The cotton may also be mordanted by working either in stannic chloride or nitro-muriate of tin, 4°—8° Tw., wringing out and passing afterwards into a cold solution of sodium carbonate, 4° Tw., and washing.

Very good results are obtained by fixing the stannic mordant on the fibre by means of tannin matters.

If it is desired to mordant with aluminium, work the cotton in cold basic aluminium sulphate, 4°—6° Tw., and fix by means of phosphate or silicate of soda.

Good chocolate or violet brown shades are obtained by mordanting the cotton with pyrolignite of iron, 4°—6° Tw., then passing into a cold dilute solution of ammonia, and afterwards dyeing with Camwood instead of Barwood, because of its greater solubility and colouring power.

By using a small proportion of "red liquor" with the iron mordant nice reddish-brown colours are obtained.

273. *Application to Wool.*—Rich claret-brown shades are obtained if wool is mordanted with 0·5—2 per cent. *bichromate of potash*, and then dyed in a separate bath with 40—80 per cent. of dyewood. Camwood gives the bluest and Sanderswood the yellowest shades, Barwood holding an intermediate place in this respect. The colouring power of Camwood is about three or four times stronger than that of the other woods.

Owing to the slight solubility of the colouring matter of these dyewoods, they are extremely well adapted for the "stuffing and saddening" method of dyeing, with this and other mordants.

The wool is boiled for 1—2 hours with 40—80 per cent. of dyewood, by which it acquires a very full brownish-red colour. It is then boiled either in the same or preferably in a separate bath, with 2 per cent. of bichromate of potash for half an hour.

The shades thus produced are all deeper and bluer than those obtained by the mordanting and dyeing method; especially is this the case with Camwood, which yields quite a purplish colour. By whichever method Camwood is applied, the addition of sulphuric acid either to the mordant or dye-bath is injurious. In practice it is certainly added to the stuffing bath, but its office is probably to neutralise the alkalinity of the scoured wool or of the calareous water.

With *aluminium mordant* and employing the "mordanting and dyeing" method a dull brownish-red, very similar to a Madder red, is obtained.

Mordant the wool with 1—6 per cent. of aluminium sulphate with 2—8 per cent. of tartar; wash and dye in separate bath for 1½—2 hours at 100° C. with 40—60 per cent. of Camwood. With the smaller amounts of mordant indicated, the red produced approaches in tone of colour that given by boiling the wool with Camwood without any previous mordanting, being only slightly bluer. By using the larger amounts of mordant the colour is lighter and yellower.

The best method, however, of applying the aluminium mordant is that of "stuffing and saddening"; first, boil the wool with Camwood (20—80 per cent.), and afterwards with 10 per cent. of aluminium sulphate in a separate bath. The reds thus produced are brighter, bluer, fuller, and more level than those obtained by the "mordanting and dyeing" method. Even when such a small amount as 10 per cent. of Camwood is employed, the pink produced is perfectly level.

Camwood gives the deepest and bluest shade of red. Barwood and Sanderswood give yellower and brighter reds, those of Sanderswood possessing the yellowest tone.

Somewhat brighter and more bluish shades of red are obtained by mordanting with 0·5—1 per cent. *stannous chloride* and 2—16 per cent. tartar, instead of with alum and tartar, and dyeing afterwards. The colours, however, lack intensity. An excess of mordant either discharges the colour or gives dull-brown shades.

The amount of tartar required in the foregoing method in order to give the best result is too large to admit of its adoption in practice. The "stuffing and saddening" method, however, gives even better results. Boil with the requisite amount of dyewood and sadden in a separate bath with 1—4 per cent. stannous chloride. The addition of tartar in this case is not beneficial. The colours obtained are fuller, bluer, and more level than those given by the first method.

By far the brightest and richest reds obtainable from these dyewoods are those produced when a *stannic salt* is employed as the mordant, but the amount of tartar which must also be added in order to mordant the wool sufficiently is so excessive as to exclude its being adopted in practice. By mordanting wool for $1\frac{1}{2}$—2 hours at 100° C. with 4—8 per cent. of stannic chloride solution (Sp. Gr., 1·6°) and 40—160 per cent. of tartar, then washing and boiling 1—2 hours with 40—80 per cent. of barwood, one obtains a bluish-red or crimson, very similar in shade to a peachwood and alum red, and certainly very much brighter and bluer than a madder and alum red. By reducing the amount of tartar the colour becomes yellower and lacks brilliancy and intensity. With this mordant Camwood gives a more intense red, having a purplish shade ; Sanderswood gives a yellower red.

Unfortunately none of the reds obtainable from these dyewoods withstand the action of light well ; a year's exposure suffices to bleach them entirely.

Copper sulphate is frequently used as a saddening agent with these dyewoods. The best results are obtained by saddening with 8 per cent. of copper sulphate. The colour given with 40—80 per cent. of Camwood is a good claret-brown.

Very different in colour are the bluish-reds obtained by mordanting with 2 per cent. of copper sulphate and 7—8 per cent. of tartar, and dyeing in a separate bath.

When *ferrous sulphate* is used as the mordant the best results are also obtained by the "stuffing and saddening" method. Sadden with 5 per cent. of ferrous sulphate. Good full purplish shades are produced similar to those obtained by using bichromate of potash. By mordanting with 5 per cent. of ferrous sulphate and 0—12 per cent. of tartar, good claret-browns are obtained.

MADDER.

274. This dye-stuff, which consists of the ground dried roots of *Rubia tinctorum*, was formerly one of the most

valued and most largely employed. It has now been more or less entirely displaced by the coal-tar derivative Alizarin and allied colouring matters.

275. *Application to Cotton.*—Madder and its commercial preparation Garancine, were formerly used by the cotton dyer for the purpose of obtaining the red colour so well known as Turkey-red, a colour remarkable for its great brilliancy and fastness both to light and to boiling alkaline solutions. The chief interest attaching to Turkey-red is the characteristic preparing of the cotton with oil previous to mordanting and dyeing, and to this, indeed, it owes its special qualities. The displacement of Madder by Alizarin in Turkey-red dyeing has not necessarily brought about any material changes in the mode of carrying out this preliminary oiling process, so that the Emulsion and Steiner's processes (*see* pp. 427, 438) may be taken as representing essentially the method of dyeing Turkey-red adopted in the days when Madder was employed, substituting merely an equivalent amount of ground Madder for the Alizarin.

276. *Application to Wool.*—When wool is boiled with Madder it acquires a pale brown or drab colour, and although this can only be considered a stain, this simple method of application has been adopted in practice.

By mordanting the wool previously with 3 per cent. of *bichromate of potash*, good reddish-browns are obtained. The addition of 1 per cent. of sulphuric acid, or 9 per cent. of tartaric acid, gives a darker colour. By the "single-bath method" fairly good colours are obtained; they are, however, yellower and not so deep as those yielded by the ordinary method.

For red, the wool is mordanted with *aluminium sulphate* and tartar, and dyed with Madder in a separate bath.

Mordant the wool with 6—10 per cent. of aluminium sulphate and 5—8 per cent. of tartar. Dye with 60—80 per cent of Madder. Begin the dyeing at 40° C., and raise the temperature of the bath gradually to 80°—100° C. in the course of one hour, and continue the dyeing about one hour longer. Wash and dry.

The shade thus produced is a brownish-red. It may be made considerably brighter, and of an orange tone, by adding a small proportion of stannous chloride solution along with the aluminium sulphate and tartar; or instead of this, the stannous chloride may be added to the dye-bath towards the end of the operation.

The gradual raising of the temperature of the dye-bath is essential in order to develop the full colouring power of the Madder. If the bath is allowed to cool considerably or frequently during the progress of the dyeing, even though the correct temperature is continually re-established, there is a loss of colouring power. If the water or Madder used, is deficient in lime, brighter and fuller shades are obtained by an addition to the dye-bath of 1—2 per cent. (of the weight of Madder employed) of ground chalk, or acetate of lime.

This addition is useful with Dutch and Alsatian madders, since these are naturally deficient in lime. The addition too of a small proportion of tannin matter along with the Madder serves to exhaust the bath more fully and to give deeper shades. Add Sumach, say, to the amount of one-tenth of the weight of Madder employed. Avoid an excess, since it gives a poor weak colour.

Brighter shades are obtained by employing the lower temperature given (80° C.) and prolonging the dyeing process, because in this case the yellow and fawn-coloured principles of the Madder are not so readily fixed.

After dyeing and washing, the colour may be made somewhat brighter by working the wool for a short time at 70° C. in a bath containing either a small proportion of soap solution, or of a decoction of bran.

With thick woollen materials it happens sometimes that the colour does not penetrate sufficiently. To overcome this defect it is usual to add a small portion of Madder to the mordanting bath, so that at least some of the colouring matter of the Madder may penetrate to the centre of the fabric before it is precipitated and fixed by the mordant. It is quite possible, indeed, to dye light shades with the Madder and mordant in the same bath, but this method is not applicable if the fullest and richest colours are required.

Under the most favourable conditions a Madder red on wool is by no means brilliant, and not to be compared in this respect with Cochineal scarlet. It is, however, a fast and permanent colour, and withstands the action of light and milling with soap extremely well.

Since the introduction of artificial Alizarin, fast reds should be dyed with this colouring matter in preference to Madder, since brighter colours are obtained at a less cost

Wool mordanted with 8 per cent. of *stannous chloride* and 4 per cent. of tartar, and dyed in a separate bath, acquires a fine orange colour. In single-bath use 4 per cent. $SnCl \cdot 2H_2O$ and 2 per cent. tartaric acid.

With *copper sulphate* and tartar, brown-colours are obtained; with ferrous sulphate and tartar, darker browns. Use two-bath method; single-bath method is also applicable.

277. *Application to Silk.*—Notwithstanding the general fastness of the colours produced by Madder, owing to their want of brilliancy this dye-stuff is comparatively little used in silk-dyeing.

For red the silk is mordanted as usual with *alum* by steeping over-night in a cold concentrated solution. Wash well and dye in a separate bath with 50 per cent. of finely ground Madder. Begin dyeing at a low temperature and raise it gradually to 100° C. The addition of bran to the bath tends to give brighter colours. For the purpose of obtaining a fuller colour one may also add to the dye-bath a small percentage of Sumach. After dyeing, wash, then brighten in a boiling solution of soap to which a small percentage of stannous chloride has been added, and wash well.

By mordanting with *ferrous sulphate*, either alone or after a previous mordanting with alum, violet and brown shades may be obtained.

COCHINEAL.

278. This colouring matter consists of the dried insect *Coccus cacti*, largely cultivated in Mexico.

It is little used in cotton-dyeing, except by the calico-printer. Formerly much employed in silk-dyeing, it has now been almost entirely replaced by the use of various aniline-reds, while in wool-dyeing since the introduction of the azo-reds its use has become more and more limited.

279. *Application to wool.*—Wool mordanted with 2 per cent. of *bichromate of potash*, and dyed in a separate bath with Cochineal, gives a good purple colour. The addition of sulphuric acid to the mordanting bath, even to the extent of 3 per cent. of H_2SO_4 168° Tw., makes the colour darker.

Two different shades of red are obtained from Cochineal, namely, a bluish red, called *crimson*, and a yellowish or fiery red, called *scarlet.*

280. **Cochineal Crimson** is obtained by mordanting the wool with 4—8 per cent. *aluminium sulphate* and 5 per cent. of tartar, and dyeing in a separate bath with 8—15 per cent. of Cochineal. The addition of lime salts to the dye-bath is not beneficial. Fairly good shades are obtained in a single bath by using 6 per cent. of aluminium sulphate and 4 per cent. of oxalic acid or 6 per cent. of potassium oxalate. Cochineal crimson can, however, be obtained in a variety of ways.

One method is to dissolve about 5 per cent. of alum, and 2½ per cent. of tartar in an old Cochineal-scarlet bath, and boil the wool about one hour in it; then dye at the boil for half an hour in a separate bath, with 10—15 per cent. of Cochineal. The following table gives the proportions of other materials which may be employed:

	Tartar. per cent.	$SnCl_2$ (crystals) per cent.	$SnCl_4$ (crystals) per cent.	Alum. sulphate per cent.	Cochineal. per cent.	Wool.
No. 1.	6	3	3	10	8 to 15	100
„ 2.	4	2	1·5	0	„	„
„ 3.	1	0	1	5	„	„

Boil 1—1½ hour with the mordants, and dye in a separate bath with the Cochineal for 20—40 minutes at 100° C.

Good crimsons may also be obtained in one bath by boiling the wool for ½—¾ of an hour with the aluminium sulphate and tartar, then removing it temporarily to add the ground Cochineal, boiling a few minutes, and finally re-entering the wool and boiling ½—¾ of an hour longer. A certain proportion of the colouring matter always remains precipitated in the bath and is lost by this method.

In order to modify the shade of crimson and make it still bluer, a small amount of carbonate of soda or liquid ammonia is sometimes added to the dye-bath towards the end of the dyeing operation, or the goods are washed in water and made slightly alkaline by the addition of a little lime-water. Other modifications of shade are obtained by adding to the dye-bath varied proportions of Ammoniacal Cochineal, Orchil, or Cudbear; these, however, produce a colour which is not so fast towards light.

Ammoniacal Cochineal is frequently used along with ordinary Cochineal for the production of rose-pinks, *i.e.*, bluish shades of pinks.

Cochineal crimson obtained by using aluminium mordant is tolerably fast to light, and also to milling with soap and weak alkaline carbonates.

281. **Cochineal Scarlet.**—The ingredients generally used in obtaining this colour are Cochineal, a stannous salt, and cream of tartar, or oxalic acid. Two distinct methods for its production may be adopted, (1) the wool is first mordanted with the stannous salt and tartar, and then dyed in a separate bath with Cochineal; (2) the mordanting and dyeing are performed simultaneously in one and the same bath.

First Method.—Mordant the wool for 1—1½ hour, with 6 per cent. of stannous chloride (crystals) and 5 per cent. of cream of tartar, and wash. Dye with 5—12 per cent. of ground Cochineal for 1—1¼ hour. In order to obtain level shades, enter the wool both in the mordanting- and dye-bath at about 50° C. and raise the temperature gradually to the boiling point. If 3 per cent. of the stannous chloride is replaced by its equivalent of stannic chloride, the colour is yellower and more brilliant (Liechti). The addition of lime salts to the dye-bath is injurious.

Second Method.—Fill the dye-bath half full of water, add 6—8 per cent. of oxalic acid, 6 per cent. of stannous chloride, and 5—12 per cent. of ground Cochineal; boil up for 5—10 minutes, then fill up the dye-bath with cold water. Introduce the woollen material, heat up the bath to the boiling point in the course of $\frac{3}{4}$—1 hour, and boil $\frac{1}{2}$ hour. Potassium oxalate may replace oxalic acid; or one may use with advantage the mixture of stannous and stannic chloride with tartar as given above.

By this "single-bath method" the dye-bath is not exhausted as in the first method; a portion of the colouring matter always remains in the bath in combination with the mordant as a yellowish flocculent precipitate. The unexhausted bath may, however, be utilised for one or two succeeding lots of material, by merely replenishing it with further quantities of the several ingredients.

In practice many modifications have at one time or another been introduced into both the above methods. In the first, for example, the mordant has been divided, adding a portion only, to the actual mordanting bath, and the remainder to the dye-bath along with the Cochineal. This division has extended either to both tartar and stannous chloride or to one of these only. Sometimes, too, the Cochineal has been divided, a small proportion being added already to the mordanting-bath. Washing between mordanting and dyeing, not being absolutely essential, has been omitted. The temperature and duration of mordanting and dyeing have varied greatly; and other stannous and stannic salts, with the addition of other assistants than tartar, have been employed. The changes rung on the variations possible in the second method have been almost equally numerous.

Comparing the two methods, experiment shows that, with an equal expenditure of ingredients, the first method gives a blue shade of red possessing both purity and intensity of colour. The single-bath method gives a yellower and more brilliant scarlet. This method is on the whole the more advantageous, and is the one generally adopted.

When the single-bath method is employed, comparatively little difference is produced by dividing the mordant and reserving a portion to be added along with the Cochineal during the second period of the process. If the addition is mainly or entirely confined to the first or mordanting period, the scarlet obtained is slightly more intense and yellower.

Without the use of tartar a poor bluish shade of red would be obtained. Addition of tartar up to 8 per cent. increases the intensity and yellowness of the colour.

A deficiency of tin mordant gives also a dull bluish-red, while an excess makes the scarlet paler.

As a rule, stannous chloride is not employed in the crystalline state—*i.e.*, as "tin-crystals"—but in the form of an acid solution, namely, as "double or single muriate of tin."

The presence of a moderate excess of free hydrochloric acid in these solutions has the following advantages:—

1. The mordant is thereby rendered less sensitive to decomposition, and is better able to penetrate thick, closely-woven or hard-spun material before any deposition of mordant takes place. The material thus becomes more thoroughly mordanted throughout its mass, the ultimate colour is not so much confined to the surface, and the material appears dyed through.

2. The free acid present, acts beneficially by retaining the coloured lake already alluded to longer in solution, so that the wool acquires a deeper shade than it would otherwise.

3. The presence of free acid in the dye-bath is absolutely essential, when a calcareous or otherwise alkaline

water is employed, unless the latter is previously neutralised ; or when after scouring the wool with weak alkaline solutions the washing has been insufficient. Without the free acid, the mordant would be precipitated in the bath to a greater or less degree, according to the alkalinity of the water, and the scarlet would either be of a weak, dull-bluish shade, or might not even be produced at all.

In dyeing Cochineal scarlet, therefore, an acid condition of the bath is essential to the production of a satisfactory colour. A large excess of free acid, however, must be avoided, otherwise the colour lacks intensity.

Other salts of tin, known as Tin Spirits, Scarlet Spirits, &c., are often used instead of those already given. The first-mentioned solution, or "nitrate of tin," is much used by dyers. The scarlet it yields has a decided yellow shade, owing probably to the action of the nitric acid liberated during the mordanting process. In this respect, therefore, it is equivalent to an extra addition of tartar.

Although stannic chloride, when used in conjunction with tartar and Cochineal, yields fairly good scarlets, these cannot compare in brilliancy with those obtained by the use of a mixture of stannous and stannic chloride.

The presence of a certain amount of stannic salt along with stannous chloride is said to be beneficial in preventing the production of so-called "tin spots," *i.e.*, dark-looking or almost black spots, which sometimes occur irregularly throughout the scarlet-dyed fabric. These spots consist of anhydrous stannic oxide, produced from the hydrate stannous oxide during the boiling. The use of oxalic acid acts beneficially in the same direction.

In order to obtain bright yellow shades of scarlet, it is usual to add a small proportion of some yellow colouring matter along with the cochineal. Flavin, or Young Fustic, are generally used for this purpose. Persian Berries are occasionally used, but they are more expensive.

Cochineal red on wool must be considered as very fairly fast to light. Its principal defect is that by the action of weak alkalis, soap, &c., it acquires a duller and more bluish shade of colour. Excessive milling must therefore be avoided whenever cochineal red is present in the goods. By rinsing the goods afterwards in water acidified with acetic acid, the bright tone is more or less restored. Cochineal is always preferable to an Azo Red for dyeing yarn intended to be woven along with other white or delicately-coloured yarns in goods which require to be scoured or milled. Cochineal red does not "bleed" and stain the neighbouring fibres like the Azo reds.

The dye-baths used for Cochineal scarlets should be either of wood, stone, or block-tin. Iron and copper ones should be rigorously avoided, since the acidity of the bath causes a small quantity of these metals to be dissolved, and the colour produced is dull.

A piece of clean block-tin placed in a copper dye-bath obviates this defect, no copper being then dissolved.

Wool mordanted with 10 per cent. of *copper sulphate*, and dyed in a separate bath with Cochineal, gives a reddish-purple or claret colour. The addition of tartar to the mordanting bath is not beneficial.

With *ferrous sulphate* as the mordant, very good purplish-slate or lilac colours can be obtained. Mordant with 8 per cent. ferrous sulphate, and 20 per cent. tartar, and dye in separate bath. In single bath use 4 per cent. ferrous sulphate and 4 per cent. potassium oxalate.

282. *Application to Silk.—Crimson.* Mordant the silk by working for half an hour, then steeping over-night in a concentrated solution of alum. Wash well, and dye in a fresh bath containing a decoction of 40 per cent. of Cochineal. Enter the silk at a low temperature, and heat gradually to 100° C.

Scarlet. After boiling-off and washing, the silk is first slightly dyed or grounded with yellow, by working it for a quarter of an hour at 50° C. in a weak soap bath containing about 10 per cent. of Annatto, it is then well washed. For darker shades of yellow use no soap, and dye at 90° C.

Mordant the silk by working it for half an hour and then steeping it over-night in a cold solution of 40 per cent. of nitro-muriate of tin. Wash and dye in a fresh bath, with a decoction of 20—40 per cent. of Cochineal, and 5—10 per cent. of cream of tartar. Enter the silk at a low temperature, and heat gradually to 100° C. Brighten in a fresh bath of cold water, slightly acidified with tartaric acid. Very good results are obtained by adopting the method found most advantageous in wool-dyeing, namely, dyeing in a single bath with Cochineal, stannous and stannic chloride, with addition ot tartar.

With the use of iron mordants very fine shades of lilac may be obtained on silk, with Cochineal.

283. Lac-dye Red (*Wool*).—Lac-dye is used for obtaining reds similar to those yielded by Cochineal, and the methods adopted are essentially the same as those already described. Owing to the presence of a large excess of mineral and resinous impurities, Lac-dye yields its colouring matter to water less readily than Cochineal; hence, twelve hours or so before it is added to the dye-bath, it should be ground and made into a paste with the tin solution to be employed, sometimes with the addition of a little free hydrochloric acid. This preliminary treatment softens the Lac-dye, dissolves part of the mineral matter with which the colouring matter may be combined in the form of a lake, and thus renders it more soluble in the dye-bath. With the exception of this slight deviation, the dyeing is performed in exactly the same manner as with Cochineal.

Lac-dye reds are less brilliant than Cochineal reds, but possess greater intensity. They are also considered to be somewhat faster to light and wear, and to the action of milling with weak alkalis. Hence Lac-dye is frequently used in conjunction with Cochineal, in order to take advantage of the good qualities of both, and thus obtain a colour which combines fastness and brilliancy. To this end the two dye-stuffs may be added to the same dye-bath; or better still, the material is first dyed with

Lac-dye and afterwards with Cochineal, in a separate bath.

ORCHIL.

284.—Orchil paste, Orchil extract, and Cudbear are prepared from certain lichens by submitting them to a process of oxidation in the presence of ammonia. They are still much used in the dyeing of compound shades on wool and silk. Their colouring matter (Orceïn) dyes best in a neutral bath, but it possesses the very useful property of dyeing either in a neutral, slightly alkaline, or slightly acid bath, and the colours have an intensity or body not readily obtainable by means of its rivals among the coal-tar colours, chief among which is Fast Red or Roccelline. The colour is not fast to light.

Orchil is not applicable in cotton-dyeing, and for wool and silk no mordants are required.

Application to Wool.—Dye in a neutral bath, or with a slight addition of sulphuric acid, or of soap solution.

Application to Silk.—Dye in a bath containing soap solution, or boiled-off liquor, with or without the addition of acetic or sulphuric acid. The colour produced is a bright bluish-red or magenta.

ANNATTO.

285.—This colouring matter is obtained from the pulp surrounding the seeds of *Bixa orellana.* Owing to the fugitive character of the red or orange colour which it yields, its employment is very limited, and is chiefly confined to silk-dyeing. A short time before it is required for use, it must be dissolved by boiling it with a solution of carbonate of soda.

Application to Cotton.—Work the cotton in a hot solution of Annatto, containing soap or carbonate of soda. Pale colours are dried direct from the dye-bath; dark colours should be rinsed slightly in a cold soap solution to remove excess of alkali from the fibre. By passing the dyed cotton through water slightly acidulated with sulphuric acid or alum, the colour assumes a redder tint.

Application to Wool and Silk.—Pale shades are dyed at 50° C., with the addition of soap to the bath; dark shades are dyed at 80°—100° C., without any addition.

SAFFLOWER.

286.—This dyestuff consists of the dried florets of the composite flower of *Carthamus tinctorius.* Previous to being used by the dyer the commercial product should be well washed with cold water to remove the worthless yellow colouring matter present. It is best to use the so-called Safflower-extract. Safflower finds a very limited use in the dyeing of cotton yarn, thread, and tape. The bright pink colour obtained is extremely fugitive.

Application to Cotton.—To ensure even dyeing the cotton is first worked for some time in a cold carbonate of soda solution of the colouring matter; it is then removed from the bath, and the solution is slightly acidified with sulphuric, acetic, or tartaric acid. The cotton is again introduced, and worked about until the bath is exhausted. The real dyeing only takes place in the acid bath. The dyed cotton is afterwards rinsed in water slightly acidified with acetic acid or cream of tartar, and dried in a cool, dark place.

Silk may be dyed in a similar manner.

CHAPTER XV.

YELLOW COLOURING MATTERS.

WELD.

287.—Weld consists of the plant *Reseda luteola.* It is principally used in wool- and silk-dyeing, for producing yellow and olive colours.

288. *Application to Cotton.*—The yellow colours obtained on cotton from this dyestuff are of little or no importance, since they are not fast to soap.

Chromium mordants yield yellowish olives, very fast to soap and light. The addition of calcium acetate to the dye-bath is beneficial.

With *aluminium* mordants yellows are obtained, but they possess no particular brilliancy.

Work the cotton in aluminium acetate 4°—6° Tw. (Sp. Gr. 1·02—1·03), and fix in a separate bath with phosphate or silicate of soda; wash and dye for $\frac{1}{2}$—$\frac{3}{4}$ of an hour at 60° C. A slight addition of acetate of copper to the dye-bath makes the shade more orange.

With *stannic* mordants the yellows produced are slightly faster to soap, and somewhat more orange in tone.

Pyrolignite of iron as the mordant, with or without the additional use of aluminium acetate, and fixed by means of silicate of soda, gives various shades of olive.

Greens are obtained by mordanting with aluminium, and dyeing with a mixture of Weld and Logwood, or by first dyeing the cotton an indigo-vat blue, afterwards mordanting with aluminium acetate, or a stannic salt, and dyeing with Weld.

289. *Application to Wool.*—The use of Weld in woollen-dyeing is limited, because it is of low colouring power and requires two baths, and because the fastness and purity of the yellow colour are not generally recognised.

Wool mordanted with 2 per cent. of *bichromate of potash*, and dyed in a separate bath with 60 per cent. of Weld, gives an olive-yellow or old-gold shade. The addition of sulphuric acid to the mordanting bath is not beneficial. The addition of 3 per cent. chalk to the dye-bath adds intensity to the colour.

To produce Weld yellow, mordant the wool by boiling it 1—2 hours with 4 per cent. of *aluminium sulphate*, wash and dye in a separate bath with a decoction of 50—100 per cent. of Weld, for 20—60 minutes, at 80°—90° C.

The dye-bath is prepared immediately before introducing the mordanted wool, the chopped Weld being enclosed in weighted bags, and boiled with soft water only, for $\frac{1}{2}$—1 hour, then add 4 per cent. chalk before dyeing.

The colour thus obtained is a yellow comparatively free from any tinge of redness. Its fastness to light and to milling with soap and weak alkalis is very satisfactory; indeed, it must be considered as superior to all other natural yellow colouring matters in these respects.

The addition of 5 per cent. tartar to the mordanting bath is beneficial, but excess makes the colour dull. The addition of 2 per cent. of stannous chloride gives brilliancy and fastness to the colour produced.

The addition of 4 per cent. of chalk to the dye-bath gives a yellow, which possesses greater intensity but less purity. The addition of calcium acetate has the same effect as that of chalk, but in a less degree.

Brighter yellows are obtained by mordanting with 8 per cent. of stannous chloride instead of with aluminium sulphate.

By adopting the "single-bath" method similar to that given for Cochineal scarlet, very good bright yellows are obtained.

Wool mordanted with 6 per cent. of *copper sulphate*, and dyed in a separate bath with Weld, gives a yellowish olive colour. The addition of tartar to the mordanting bath is not beneficial. Add 2—8 per cent. chalk to the dye-bath.

Wool mordanted with 4 per cent. of *ferrous sulphate* and 3 per cent. of tartar, and dyed in a separate bath with the addition of chalk, gives good olive colours.

290. *Application to Silk.*—Of all the natural yellow colouring matters, Weld is the most important to the silk-dyer, since the colours it yields are relatively fast to light and slight soaping. It is principally used for dyeing yellow, olive, and green.

For yellow, the silk is mordanted in the usual manner with alum, washed and dyed in a separate bath at 50°—60° C. with a decoction of 20—40 per cent. of Weld.

A small quantity of soap solution is added to the dye-bath, in order to ensure even dyeing. The amount to be added increases with the degree of hardness of the water, and the percentage of weld employed; in any case, the addition of too much should be avoided. It is, of course, better to correct the water previously. After dyeing, the colour is brightened by working the silk for ten minutes in a fresh soap bath to which, in order not to impoverish the colour, a little decoction of Weld has been added. Wring out without washing. If scroop is required, the silk is washed, and then worked for ten minutes in water slightly acidulated with acetic acid.

It is essential to the production of bright yellows that the aluminium salt used be absolutely free from iron. The best Weld to employ is the short French Weld from Cette, and the purest yellows are obtained from the first and second decoctions of the flower portion of the stem. The root portion contains a little tannin matter, which tends to dull the colour.

Dark shades of yellow are dyed in the same way, using proportionately more Weld (50—70 per cent.). The addition of soap to the bath is not necessary, but it is advisable to keep the temperature somewhat lower. For very dark shades it may be necessary to dye in two Weld baths. Very often, before wringing, the silk is worked at 60° C. in a strong soap bath, containing a little Annatto, in order to give a slightly more orange tint, as well as additional brilliancy. Full orange colours are produced by first grounding with Annatto, afterwards mordanting with alum, and dyeing with Weld.

OLD FUSTIC.

291. This dyestuff consists of the wood of *Morus tinctoria*. It is principally used in woollen-dyeing, also to a limited extent in silk-dyeing.

292. *Application to Cotton.*—Old Fustic is but little used by the cotton dyer, the colours it produces on cotton not being fast to soap.

The same methods of application as for Weld may be employed.

293. *Application to Wool.*—In the heavy woollen trade,

this is perhaps the most largely used of all the natural yellow colouring matters, but principally along with other dyewoods for the production of various compound shades, *e.g.*, browns, olives, drabs, &c.

With *bichromate of potash* as the mordant, it gives a pleasing brownish or olive-yellow colour (old gold).

Boil the wool for 1—1½ hour with 3—4 per cent. of bichromate of potash, wash, and dye in a separate bath for 1—1½ hour at 100° C. with 20—80 per cent. of ground Old Fustic. By increasing the amount of mordant deeper colours are obtained, but it is not advisable to use more than that indicated.

The addition of tartar or sulphuric acid to the mordanting bath is not beneficial.

With *aluminium* mordant Old Fustic gives yellow colours, which differ in brightness, according as the dyeing is done in one or two baths. The "single-bath" method gives the brightest shades. Dye for 1—1½ hour with 4 per cent. of aluminium sulphate, 2 per cent. of oxalic acid, and 20—40 per cent. of Old Fustic, at 80°—100° C. The addition of tartar intensifies but dulls the colour.

When two baths are employed, mordant the wool for 1—1½ hour with 8 per cent. of aluminium sulphate, wash, and dye in a separate bath for ½—¾ hour, at 80°—90° C., with 20—40 per cent. of Old Fustic. Here, too, the addition of tartar to the bath is not beneficial. By using 2—3 per cent. of stannous chloride along with the aluminium sulphate, much brighter colours are obtained.

The brightest and fastest yellows obtainable from Old Fustic are produced with the use of a *stannous* mordant. Mordant the wool 1—1½ hour with 8 per cent. of stannous chloride (crystals), and 8 per cent. of tartar; wash, and dye in a separate bath for 30—40 minutes, at 80—100° C., with 20—40 per cent. of Old Fustic.

Very bright yellows are better obtained by adopting the "single-bath" method given for Cochineal scarlet, possibly because then the lime compound of the colouring principle "morin" is decomposed. Use 40 per cent.

of Old Fustic, 8 per cent. of stannous chloride, 4 per cent. of tartar, and 2 per cent. of oxalic acid. By using less mordant fuller colours are obtained, but they are not so bright.

Prolonged dyeing must always be avoided, especially when dyeing at 100° C., or when two baths are employed, otherwise the yellows become dull and brownish, owing to the presence in Old Fustic of a considerable amount of tannin matter. This effect can be obviated to a large extent by adding a solution of glue to the dye-bath, in the proportion of 4—8 per cent. of the weight of Old Fustic employed.

Stannic chloride, in conjunction with Old Fustic, gives light-brown or fawn colours, and is not a suitable mordant.

All the yellows obtained from Old Fustic change to a dull brownish colour after one month's exposure to sunlight, but they bear milling with soap and weak alkalis fairly well.

With *copper sulphate* mordant Old Fustic yields olive colours. Either the "mordanting and dyeing" method, or the "single-bath" method may be adopted. Use 4—6 per cent. of copper sulphate and 0—4 per cent. of tartar.

With 8 per cent. *ferrous sulphate* and 3 per cent. tartar, darker olives are obtained. The "single-bath' method gives good and level colours. Use 4—8 per cent. ferrous sulphate, without the addition of tartar.

294. *Application to Silk.*—Old Fustic is still used in silk-dyeing for the purpose of obtaining various shades in green and olive. It is now seldom or never used for dyeing yellows, since they cannot compare in brightness with those derived from Weld, or from some of the coal-tar colouring matters.

It is occasionally used in conjunction with other colouring matters for obtaining compound colours, or for modifying the shade of certain blacks.

If required for a light yellow, the silk is worked for $\frac{1}{4}$—$\frac{1}{2}$ hour, at 50°—60° C., in a bath containing 16 per cent. of alum, and a decoction of 8—16 per cent. of Old Fustic.

For dyeing a darker yellow—required, *e.g.*, when producing in conjunction with indigo-vat blue the so-called "fast-green"—the silk is mordanted with alum, washed, and dyed for about an hour, at 50°—60°, with a decoction of 50—100 per cent. of Old Fustic, and then washed.

The colour may be rendered brighter and faster by working the silk afterwards in a cold solution of nitro-muriate of tin, at 4° Tw., for an hour, and then washing.

QUERCITRON BARK.

295.—This dyestuff consists of the inner bark of *Quercus tinctoria.* Its dyeing properties are so similar to those of Old Fustic that the same methods of application may be used for both.

296. *Application to Cotton.*—The colours produced on cotton by means of this dyewood are very similar to those obtained from Weld, and the same methods of application may be adopted. Quercitron yellow on cotton when dyed with Malachite Green gives very good yellowish-green shades.

297. *Application to Wool.*—With bichromate of potash mordant, Quercitron Bark gives somewhat redder olive-yellows than those yielded by Old Fustic. Mordant with three per cent. of *bichromate of potash,* without the addition of sulphuric acid or tartar, and dye in a separate bath. The *aluminium* yellows are paler, while those produced by stannous chloride are very much brighter and more orange in shade than the corresponding Old Fustic colours.

With *stannic chloride,* Quercitron Bark gives a very pale buff colour.

In all cases prolonged dyeing is injurious, and gives dull shades. The addition of glue solution to the dye-bath is beneficial, since it precipitates the tannin matter invariably present.

The resistance of Quercitron Bark colours to light and milling is about the same as that of those yielded by Old Fustic. It is not extensively used in woollen dyeing, having been largely supplanted by Flavin.

298. *Application to Silk.*—Quercitron Bark is seldom used alone in silk-dyeing. If required, it may be applied in the same manner as Weld or Old Fustic.

Its principal use is for obtaining a dead-black, a small quantity of its decoction being added to the Logwood dye-bath.

FLAVIN.

299.—This dyestuff is a preparation of Quercitron Bark, and consists essentially of "quercetin." "Quercitrin" may also be present in some products. It has occasionally been sold under the name "Aurantine." The advantages which Flavin has over Quercitron Bark are, that it is very much stronger in colouring power, and being free from tannin matter it yields brighter shades. A good quality of Flavin may possess sixteen times the colouring power of Quercitron Bark, but very inferior qualities are frequently met with. So-called "Patent Bark," prepared by boiling ground Quercitron Bark with sulphuric acid, is an excellent substitute for Flavin in wool-dyeing.

Flavin is not used in cotton-dyeing.

300. *Application to Wool.*—When employed for yellow, tin mordants, with or without the addition of aluminium sulphate, are used. With aluminium mordants alone, comparatively pale yellows are produced. With stannous mordants the yellows are very much richer, and of a more orange tone. With stannic mordant pale yellowish buffs are produced.

In dyeing Flavin yellows it is most advantageous to mordant and dye in one bath, after the manner recommended for dyeing Cochineal scarlet. By this means, brighter colours are obtained. Boil the wool for $\frac{1}{2}$—$\frac{3}{4}$ of an hour with 4—8 per cent. of stannous chloride (crystals), and 0—4 per cent. of tartar; take out the wool temporarily; add 1—8 per cent. of Flavin; boil five to ten minutes; re-enter the wool, and continue boiling for half to one hour. It is well to mix up the Flavin with a little hot water to form a smooth paste, before adding it to the dye-bath, since it tends to form lumps not readily wetted and dissolved, if thrown into the bath in the dry state.

Increase of stannous chloride adds intensity and redness to the colour.

Acid solutions of stannous chloride or nitrate of tin may be used instead of stannous chloride crystals.

Increase of tartar reduces the intensity, brilliancy, and redness. The tartar may be partly or entirely replaced by 2—4 per cent. of oxalic or tartaric acid, when, indeed, brighter shades result.

Increase of Flavin adds intensity and redness. With 1 per cent. of Flavin the shade produced is a bright canary-yellow; with 8 per cent. it is a bright orange.

Flavin yellows and oranges on wool, obtained by means of stannous mordants, are among the brightest that can be produced from either natural or artificial colouring matters.

With regard to their fastness to light and milling with soap and dilute alkalis, they behave the same as those of Quercitron Bark and Old Fustic, becoming brownish.

Flavin is much used along with Cochineal for dyeing scarlet.

301. *Application to Silk.*—Flavin is not generally used in silk-dyeing. It may, however, be applied in the same manner as Weld.

YOUNG FUSTIC.

302.—This colouring matter consists of the wood of the sumach tree (*Rhus cotinus*).

Owing to the fugitive character of all the colours produced by this dyestuff, it is of little or no use to the cotton and silk dyer, and it would be no great loss if it disappeared from the market altogether. It was, however, much used formerly in dyeing brown colours on silk, the yarn being mordanted with alum and afterwards dyed with a decoction of Young Fustic, Peachwood, and Logwood. It still finds a limited use in wool-dyeing for the production of orange or scarlet.

303. *Application to Wool.*—Wool mordanted with *bichromate of potash* and dyed in a separate bath with Young Fustic, gives a reddish brown. The colour is much redder than that obtained in a similar manner from any other of the yellow dyewoods, with the exception of Persian Berries. Very large amounts of bichromate of potash may be used, and with good effect, but it is not advisable to employ more than 3 per cent. The addition of sulphuric acid is not beneficial.

With an *aluminium* mordant it produces a yellowish buff colour.

The brightest yellows yielded by Young Fustic are those obtained when it is used in conjunction with *stannous* mordants. With *stannous chloride* (or nitrate of tin) and tartar, and with a good quality of Young Fustic, bright orange yellows are obtained, not unlike those given by Quercitron Bark or Flavin. The same methods of dyeing and proportions of mordants employed in the case of Flavin may be adopted here, using only larger amounts of dyewood, say 20—40 per cent. of Young Fustic. With a *stannic* salt as mordant it yields a tolerably good full orange yellow, but only when prohibitory amounts of tartar are employed.

The colours yielded by the use of *copper* and *iron* mordants are olives similar to those obtained from the other yellow dyewoods.

The yellows and oranges obtained from Young Fustic are not fast to light, two or three months' exposure being sufficient to bleach the colour entirely. All except the aluminium colour withstand milling with soap and weak alkalis moderately well.

In these respects Young Fustic is not so good as any of the other natural yellow colouring matters.

PERSIAN BERRIES.

304. This colouring matter consists of the dried unripe fruit of various species of *Rhamnus;* it is not used in cotton- and rarely in silk-dyeing, although very largely in calico-printing for steam-orange, olive, green, &c.

Application to Wool.—Persian Berries are seldom used in woollen-dyeing. They seem to be excluded entirely from the heavy woollen trade, and find only a limited use in dyeing light materials for ladies' wear. The chief objection is their high price, but they are also very variable in quality.

In general dyeing properties Persian Berries greatly resemble Young Fustic, but the colours produced are very much faster.

With *bichromate of potash* mordant very good reddish browns are obtained.

With *aluminium* and *stannic* mordants only pale, unsatisfactory dull yellows are obtained. With *stannous* mordants rich yellows and oranges are obtained, which, when a good quality of Persian Berries has been employed, are equal if not superior in brilliancy to those obtained from Flavin. Use the same methods and proportions of mordants employed in the case of Flavin, but with 10—40 per cent. of Persian Berries.

When exposed to light, Persian Berry yellows gradually become brownish, but in this respect they are not different from those obtained from Old Fustic and Quercitron Bark and Flavin, and are decidedly superior to those obtained from Young Fustic. They also bear milling with soap and weak alkalis very fairly.

The action of light on the olive obtained by the use of *copper sulphate* mordant is very characteristic. The olive gradually becomes greener and increases in intensity. Even after an exposure of twelve months no fading action seems to take place. This olive is probably as fast to light as any known, and may be classed in this respect along with vat-indigo blue, &c.

TURMERIC.

305. This dyestuff is the tuber of *Curcuma tinctoria.* Notwithstanding the very fugitive character of the colour it yields, it is still much used, especially by the wool- and silk-dyer for the production of compound shades—olives, browns, &c. It gives a bright yellow colour without the aid of a mordant, but when mordants are used with it it yields other colours not unlike those obtainable from the yellow dyewoods.

306. *Application to Cotton.*—The colouring matter of Turmeric is one of the few for which cotton has naturally a strong attraction. Cotton is dyed by simply working it in a Turmeric bath heated to about 60° C. for about half an hour. The colour is not fast either to light or to alkalis; even very slightly alkaline solutions—*e.g.*, soap—change it to a reddish brown.

307. *Application to Wool.*—Dye at 60° C. without any addition. Boiling should be avoided, since the bright yellow then becomes soiled by reason of impure extractive matters entering into solution. If the wool is mordanted with aluminium or tin the colour is somewhat brighter, and in the latter case more orange. With the use of potassium dichromate and ferrous sulphate as the mordant, the colours produced are olive and brown.

Silk is dyed in the same manner as wool.

BARBERRY.

308. This yellow dyestuff is the root, sometimes the bark, of *Berberis vulgaris;* it is also sold in form of an extract. It is principally used in the dyeing of leather, but still finds a limited application in silk-dyeing.

Application to Silk.—Work the silk at 50°—60° C. in the dyewood decoction, slightly acidified with sulphuric, acetic, or tartaric acid. For dark shades the silk may be previously mordanted with stannous chloride.

CATECHU.

309. This valuable dyestuff is obtained from certain species of *Acacia*, *Areca*, and *Uncaria*, growing in India. It is largely used by the cotton-dyer for the purpose of obtaining various shades of brown, olive, drab, grey, and black. It is also extensively employed in black silk dyeing. In woollen dyeing it is little used.

310. *Application to Cotton.*—The brown colour produced on cotton by Catechu is remarkable for its fastness to light, soap, alkaline and acid solutions, and even to solutions of bleaching-powder.

For the production of Catechu brown, the cotton is worked for ½—1 hour at 80°—100° C. in a solution of 10—20 per cent. of Catechu, or, say, one containing 10—20 grams of Catechu per litre. After squeezing the cotton and allowing it to cool, it is worked for half an hour at 60° C. in a fresh bath containing 1—2 grams of bichromate of potash per litre, and is finally well washed. For very deep and full shades, the cotton is allowed to steep in the hot Catechu decoction till the latter becomes cold, before passing it into the bichromate of potash bath. The deepest shades are produced by drying the cotton after the Catechu bath. Very frequently—*e.g.*, in warp dyeing—the cotton is passed rapidly through a succession of Catechu and bichromate baths. In this process it simply becomes impregnated in the first bath with *catechin;* this in its pure state would be quite white, but in the second bath it is immediately and completely oxidised, and is said to form insoluble brown *japonic acid* within and upon the fibre. Previous mordanting of the cotton is not necessary, since the shade would be only slightly modified thereby. Mordants, however, are used when other colouring matters in the form of extract are added to the catechu bath—*e.g.*, Logwood, Alizarin, Old Fustic, &c.

With aluminium-mordanted cotton the simple Catechu colour is a yellowish brown ; with tin mordants it is rendered still yellower. Iron mordants produce the greatest change, and yield a brownish- or greenish-grey. When, however, such colouring matters as those just mentioned are also added to the dye-bath, the shades of brown and grey may be modified *ad libitum*. Indeed, the fastness of such shades varies according to the colouring matter and mordant employed in addition.

When Catechu only is used, a somewhat darker shade of brown is obtained by adding to the dye-bath copper sulphate or acetate, in the proportion of about 6 per cent. of the weight of Catechu. The intensifying of the colour is probably due to the production of basic copper chromate. This addition, however, of an oxidising agent to the dye-bath, although at first sight beneficial, is scarcely to be recommended, since it oxidises the Catechu, and thus gradually spoils the bath for dyeing subsequent lots of cotton. The object of the dyer should always be to retain the Catechu, as much as possible in the unoxidised and soluble form until the fibre is impregnated with it, and then only to submit it to an oxidising action.

The mordants above referred to may be applied before or after the bichromate of potash bath, the cotton being worked in their cold solutions at 1°—4° Tw. (Sp. Gr. 1·005—1·02), and afterwards in a bath of sodium phosphate or other suitable fixing-agent.

Numerous light shades may be obtained by a subsequent dyeing, but without using any extra mordant. In such a case, the chromed cotton is merely washed and dyed in the necessary solution of dyewood extract. The small quantity of chromic oxide which is invariably precipitated on the fibre during the operation of chroming, acts as mordant in this case.

A very usual method of obtaining the modified colours now under consideration, is to boil the cotton with a solution of Catechu to which dyewood extract has also been added, and then to sadden (preferably in a separate bath) with copper or ferrous sulphate, or both, and finally to pass into the bichromate of potash bath.

When fastness to light is not essential, the basic coal-tar colours may be employed for the purpose of modifying the original Catechu colour ; in this case the cotton is first dyed with Catechu and passed through bichromate of potash as usual, then washed, and dyed in a cold or tepid solution of the coal-tar colour. Bismarck Brown and Magenta are often employed in this way.

In practice, dyers do not always use the Catechu in the exact state in which it is imported. There is indeed a so-called "prepared cutch" in the market, made by melting Catechu with the addition of aluminium-sulphate. This product is said to possess a greater colouring power than the original Catechu.

Catechu blacks are produced by working the cotton in a hot decoction of Catechu, allowing it to steep in the bath till cold, then working it in cold nitrate of iron at 2° Tw. (Sp. Gr. 1·01), washing and dyeing in a cold or tepid decoction of Logwood, and finally passing through bichromate of potash solution.

311. *Application to Wool.*—As already stated, Catechu is very little used in wool-dyeing, although it is capable of yielding fine rich brown colours, which are fast to milling, scouring with alkaline solutions, and also to light. When used in excess it is apt to give the wool a harsh feel, and to destroy somewhat its milling properties, but where really fast browns are required, this dyestuff should certainly not be lost sight of by woollen-dyers.

The best method of applying it to wool is similar to that adopted by the cotton-dyer.

The wool is boiled for 1—1½ hour with 10—20 per cent. of Catechu, and saddened at 80°—100° C., in a separate bath for half an hour with 2—4 per cent. of copper sulphate, ferrous sulphate, or bichromate of potash. The Catechu bath, not being exhausted, may serve for dyeing fresh quantities of wool, and merely requires to be replenished occasionally with further additions of catechu decoction.

By adding to the dye-bath such other dyestuffs as

Camwood, Alizarin, extracts of Logwood, &c., numerous shades of fast brown are obtained.

312. *Application to Silk.*—The principal use of Catechu to the silk-dyer is to add weight to the silk in dyeing black. For this purpose the yellow variety (Gambier) is preferred.

Catechu is chosen instead of other tannin matters—*e.g.*, galls—for weighting, since its iron compound resists better the action of hot soap solutions in subsequent operations, and the black does not acquire such a rusty appearance.

The following is an outline of the method of its application for heavily-weighted blacks.

After boiling-off, steeping in basic ferric sulphate, and dyeing Prussian Blue, the silk is worked for an hour at a temperature of 60°—70° C., in a bath containing 100—200 per cent. of Catechu. If necessary, the silk may be left steeping over-night in the liquor without danger. When only little weighting is needed, a temperature of 50° C. is used, and the strength of the Catechu bath does not exceed 4°—5° Tw. (Sp. Gr. 1·02—1·025). At this temperature the tannin matter acts only on the silk, and weights it to the extent of 10—12 per cent., but at the temperature of 60°—70° C., the Prussian Blue already on the fibre is acted upon. A portion of the tannin matter is thus destroyed, but the rest combines with the ferrous-ferric oxide, and the weight of the silk is increased by 30—40 per cent.

The maximum weighting effect, however, is produced by the combined use of Catechu and stannous chloride. The silk is first worked in the Catechu bath for an hour at 50° C., then lifted out. After adding to the bath, and dissolving, 5—15 per cent. of stannous chloride (according to the number of previous iron baths), the silk is re-entered, and worked for 1—2 hours at 70°—75° C., or, if necessary, it may be steeped for one or two nights without injury. Exposure of the silk to the air should be avoided as much as possible, by keeping the bath filled with liquor, and the rods full of silk, and pressed closely together; otherwise the stannous salt becomes oxidised, and the silk acquires a stiff feel. The stannous chloride acts as a reducing agent, and is said to facilitate the formation of ferrous-ferric oxide, but there is, at the same time, a considerable quantity of stannic oxide fixed upon the fibre.

When no stannous chloride has been added to the Catechu bath, the latter ought to be preserved, since it is not exhausted. Old Catechu baths, indeed, give better results than new ones, both as regards weighting and colour; this is said to be due to the small quantity of iron which they contain from previous operations. If stannous chloride, however, has been added, the Catechu bath is of no further use, and can be at once thrown away.

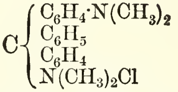
APPLICATION OF THE ARTIFICIAL COLOURING MATTERS.

CHAPTER XVI.

ANILINE COLOURING MATTERS.

a. Rosaniline Group.

313. Benzaldehyde Green.



$$C\begin{cases} C_6H_4\cdot N(CH_3)_2 \\ C_6H_5 \\ C_6H_4 \\ N(CH_3)_2Cl \end{cases}$$

This colouring matter is derived from dimethyl-aniline, and is the hydrochloride of tetra-methyl-diamido-triphenyl-carbinol. In commerce it occurs really as various salts (sulphates, oxalates, &c.), or zinc double salts of the colour-base, and is sold under a variety of names, *e.g.*, Malachite Green [$3(C_{23}H_{24}N_2\cdot HCl)2ZnCl_2\cdot 2H_2O$] (Act. Gesell. Farben Fabrik, Berlin), Solid or Fast Green [$2C_{23}H_{24}N_2\cdot 3C_2H_2O_4$] (L. Cassella & Co.), Victoria Green (Badische Anilin and Soda Fabrik), Benzoyl Green, New Green, &c. Closely allied colouring matters possessing similar dyeing properties, are those derived from *diethyl*-aniline, and known as Ethyl Green, Fast Green J, New Victoria Green OG (BASF), Brilliant Green, &c. They give yellower shades of green than those derived from *dimethyl*-aniline. In dyeing with all these greens, the temperature of the dye-bath may, if necessary, be raised to 100° C. without injuring the colour.

Application to Cotton.—Prepare the cotton with tannic acid and tartar emetic (*see* p. 230), wash, and dye in a fresh bath. The dye-solution may be cold or it may be heated gradually to a temperature not exceeding 60° C. Add the colour-solution (2—4 per cent.) gradually. The dye-bath, which is sometimes very slightly acidified with acetic acid, is not exhausted, and should be preserved for fresh lots of material.

For bright shades, the cotton may be prepared with sulphated oil and aluminium sulphate (*see* p. 236).

For yellow shades of green add to the dye-bath Auramine or other basic yellow colouring matter. One may also mordant with aluminium, fix with phosphate of soda, and dye first with Quercitron Bark and then with Benzaldehyde Green in a separate bath.

Jute is dyed with this and all basic colouring matters without being mordanted.

Application to Wool.—Dye in a neutral bath, *i.e.*, without any other addition than the colour-solution. The custom of adding soap to the dye-bath is not to be recommended, because of the formation of insoluble sticky zinc soap. An addition of at most 1—2 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), alum, or other acid salt, may be made under special circumstances. The colour shows a great tendency to rub off, and does not withstand the action of milling or of light. Better results in all these respects are obtained by mordanting the wool previously with thiosulphate of soda, according to the method given for Methyl Green (*see* p. 384).

Application to Silk.—Dye at a temperature of 50°—60° C. in a bath containing a small quantity of soap, or "boiled-off" liquor. Sometimes a little sulphuric acid is added to the bath. Wash well, brighten in a cold bath very slightly acidulated with acetic acid, and dry.

For yellow shades of green, add to the dye-bath Auramine or other basic yellow colouring matter. If Picric Acid or other acid colour is used, it must be added to the brightening bath, taking care not to use any excess of acetic acid, otherwise the green will be stripped off. It is better to dry the silk at once after brightening, in order not to remove any Picric Acid by rinsing.

314. Acid Green.—Several acid greens are met with in commerce, bearing such names as Helvetia Green (Soc. Chem. Ind., Basle), Acid Green (Poirrier), Light Green S (BASF), Guinea Green (Act. Gesell., Berlin), &c. They are sodium or calcium salts of the sulphonic acids of the base of one or other of the Benzaldehyde Greens.

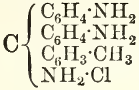
As their name implies, they require to be applied in an acid bath. Their dyeing power is less than that of the Benzaldehyde Greens, but employed with other acid colours they are extremely useful for producing compound shades. They are not suitable for dyeing cotton.

Application to Wool.—Dye with the necessary amount of colour and 2—3 times its weight of sulphuric acid 168° Tw. (Sp. Gr. 1·84) added. An addition of 10—20 per cent. of sodium sulphate may also be made if there is any tendency to uneven dyeing. Raise the temperature gradually, to near the boiling point.

Application to Silk.—Dye at a temperature of 50° C. with the addition of "boiled-off" liquor slightly acidified with sulphuric acid.

315. Alkali Green, Viridin. — This colouring matter, derived from diphenylamine by the Malachite Green process, or prepared by oxidising benzyl-diphenylamine with chloranil, is only of limited use. Being a sodium sulphonate of the colour-base, its dyeing properties are similar to those of Alkali Blue, and it is applied in exactly the same way (*see* p. 379). Pleasing greenish shades of blue may be obtained on wool by using mixtures of Alkali Blue and Alkali Green.

316. Magenta.



$$C\begin{cases} C_6H_4\cdot NH_2 \\ C_6H_4\cdot NH_2 \\ C_6H_3\cdot CH_3 \\ NH_2\cdot Cl \end{cases}$$

This colouring matter, sometimes called Roseïne, Ponceau, Rubine, &c., is usually the hydrochloride or the acetate of the organic base tolyl - diphenyl - triamido - carbinol or rosaniline. Various bye-products, containing impure Magenta, are sold under different names, *e.g.*, Cerise, Grenadine, Cardinal, Amaranth, &c. None of these yield dyes which are fast to light.

Application to Cotton.—Prepare the cotton with tannic acid, and either tartar emetic or stannic chloride (*see* p. 230), wash well, and dye in a separate bath at 45°—50° C. Add the colour solution to the bath gradually. In conjunction with other basic colouring matters, *e.g.*, Chryoïdine, Neutral Violet, &c., numerous compound shades (claret, bordeaux, &c.) can be obtained.

Brighter colours are obtained by mordanting the cotton with sulphated oil and aluminium sulphate (*see* p. 236), but they are not so fast to soap as those fixed by means of tannic acid. Both methods are applicable to all basic colouring matters.

Application to Wool.—Dye in a neutral bath. Heat gradually to 90° C. With the addition of 2—4 per cent. of soap, the colour obtained is brighter; but, in this case, the bath cannot be exhausted, and should be preserved, if possible, for subsequent lots of woollen material. This is the general mode of dyeing with all basic colouring matters.

The colour bleeds in milling, and is not suitable for "Tweed-yarns," &c.

Application to Silk.—Dye at 50°—60° C. in a weak, fresh, soap bath, adding the colour solution gradually. Wash and brighten, for yellow shades, in a bath slightly acidulated with acetic or tartaric acid; for blue shades acidify with sulphuric acid.

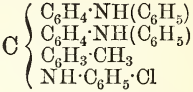
317. **Acid Magenta.**—This colouring matter is the sodium salt of the trisulphonic acid of rosaniline. It has only about half the colouring power of Magenta, and is not applicable in cotton-dyeing.

Application to Wool.—Dye in a bath acidified with 2—4 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), with the addition of 20—30 per cent. of sodium sulphate if there is any tendency to irregular dyeing. Introduce the textile material at 40° C., raise the temperature to 100° C. in 40 minutes, and boil 20—30 minutes. This is the general mode of dyeing with all similar acid colours.

Acid Magenta is much used in conjunction with other colouring matters applied in an acid bath, for dyeing compound shades. The colour it yields is decolorised by the action of alkalis, and is not suitable for goods requiring to be milled.

Application to Silk.—Dye in a bath containing "boiled-off" liquor slightly acidulated with sulphuric acid. Add the colour solution gradually.

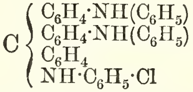
318. I. Spirit Blues: Rosaniline Blue.



$$C\left\{\begin{array}{l}C_6H_4\cdot NH(C_6H_5)\\ C_6H_4\cdot NH(C_6H_5)\\ C_6H_3\cdot CH_3\\ NH\cdot C_6H_5\cdot Cl\end{array}\right.$$

This colouring matter, in its purest form, is the hydrochloride of tri-phenyl-rosaniline. According to its purity, this blue yields shades which vary from a dull reddish-blue to a pure sky-blue. The redder shades are marked R (Dahlia, Parma Blue, &c.), while those marked 5 B and 6 B (Opal Blue, Lyons Blue, &c.) give the purer shades. Intermediate products are marked B, 2 B, 3 B, 4 B (Humboldt Blue, Imperial Blue, Gentiana Blue, &c.).

Diphenylamine Blue.



$$C\left\{\begin{array}{l}C_6H_4\cdot NH(C_6H_5)\\ C_6H_4\cdot NH(C_6H_5)\\ C_6H_4\\ NH\cdot C_6H_5\cdot Cl\end{array}\right.$$

This colouring matter, derived from diphenylamine, is considered as the hydrochloride of tri-phenyl-para-rosaniline. It is a somewhat finer but also more expensive blue.

Methyl and **Ethyl Blue.**—These are methyl and ethyl derivatives of Diphenylamine Blue, and are distinguished by the extreme purity of the greenish-blue colour which they yield.

These spirit colours are dissolved in 40—50 times their weight of methylated spirit, sometimes with the addition of a very little sulphuric acid. Use a narrow-necked vessel, and heat by placing it in hot water.

Application to Cotton.—The cotton is prepared with oleate of alumina. Work the bleached cotton in a hot (60° C.) soap bath (60—100 grams of soap per kilo. of cotton), squeeze and work in a cold bath of aluminium acetate, 8° Tw. (Sp. Gr. 1·04), and squeeze. Repeat these operations three times, and dye in a fresh bath. One may also work the soaped cotton at once in a dye-bath to which aluminium acetate has been added. Add the colour solution in small portions, and heat gradually to the boiling point. Wash well in cold water, and pass finally through a weak soap bath heated to 60° C., to which a little acetic acid has been added till it just begins to show signs of turbidity.

Cotton may also be prepared with tannic acid, and dyed in a fresh bath containing colour-solution and acidified with alum.

Application to Wool.—Dye with 1—5 per cent. of colouring matter (or more if necessary), with the addition of 4—8 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), and 10—20 per cent. of sodium sulphate. Enter the wool at 50°—60° C., heat up rapidly to 100° C., and boil half an hour, or longer if necessary. The acid and also the colour solution should be added gradually to the bath, and in small portions at a time, in order to ensure a regular colour. Instead of sulphuric acid one may also acidify with 10—12 per cent. of alum.

When the red shades of blue are used, the addition of sulphuric acid gives the best colour; with the purer blues brighter shades are obtained with the use of alum.

Owing to their insolubility, Spirit Blues are very apt to dye unevenly, but they are preferred by yarn-dyers when the goods have subsequently to be milled.

Application to Silk.—Introduce the silk into a tepid bath containing "boiled-off liquor" acidified with sulphuric acid. Add the colour solution by degrees, heat gradually to 100° C., and dye at this temperature. Wash in cold water and brighten with dilute sulphuric acid.

319. II. Soluble Blues.—The Soluble Blues generally consist of the ammonium or sodium salts of the *di-* and *tri-*sulphonic acids of Rosaniline or Diphenylamine Blues. They vary considerably in purity of colour, and are marked R, B, 2 B, 6 B, &c. The redder shades are known by such commercial names as Serge Blue, Navy Blue, Blackley Blue, &c., while those of purer tone are known as China Blue, Night Blue, Soluble Blue, Water Blue, Cotton Blue, &c.

Application to Cotton.—The cotton is prepared with tannic acid and tartar emetic, and dyed at 60°—70° C., in a separate bath, slightly acidulated with alum.

Light shades of blue are frequently dyed without any previous preparation.

The method given for Spirit Blue may also be used.

Another method recommended is to work the cotton at 60° C. in a bath containing the colour solution and 3 per cent. of stannate of soda. When the cotton is properly saturated, acidify the solution with sulphuric acid, and work ½ hour longer.

In all cases the dye-bath should be preserved, since not only is the bath never completely exhausted, but further lots dyed in the same bath have also a brighter colour.

Application to Wool.—Dye as in the same manner as with Spirit Blues.

Application to Silk.—Dye as with Spirit Blues.

320. **Alkali Blue.**—This is a special kind of Soluble Blue; it consists essentially of the sodium salt of the *mono-*sulphonic acid of Rosaniline Blue. Both red and blue shades are met with; they are marked accordingly with R, B, &c., or they have such names as Guernsey Blue, Fast Blue, Nicholson's Blue, &c. The red shades are faster than the blue shades, both to light and to the action of dilute alkalis in milling, &c.

Alkali Blues are not applicable in cotton-dyeing.

Application to Wool.—Wool must always be dyed with Alkali Blue in a slightly alkaline bath (hence the name). The wool takes it up in the form of a colourless sodium salt. The development of the colour, *i.e.*, the precipitation on the fibre of the blue-coloured mono-sulphonic acid, is effected in a separate and slightly acid bath. The water of the dye-bath should be as free from lime-salts as possible, since the lime compound of the mono-sulphonic acid is insoluble.

In dyeing wool, add to the dye-bath the amount of colour solution requisite to obtain the desired shade (say 0·5—5 per cent.), and dissolve in it also 4—8 per cent. of carbonate of soda (crystals). Introduce the wool into the bath at 40° C., heat rapidly to 80° or 100° C., and boil $\frac{1}{2}$—$\frac{3}{4}$ hour. It is then taken out, washed well in water, and transferred to a bath containing water slightly acidulated with sulphuric acid (5 per cent. of sulphuric acid, 168° Tw.). It is worked in this bath for 15—20 minutes at 60° C., until the colour is fully developed, and is then washed free from acid. If the first bath, or the *dye-bath* as it may be called, is sufficiently alkaline, the wool acquires therein only a very pale bluish tint, but on passing it into the second bath, which may be named the *acid* or *developing bath*, the blue is at once developed. The dye-bath is never exhausted, and should always be preserved. For succeeding lots of wool add proportionately less of both colour solution and carbonate of soda. Instead of carbonate of soda, borax or strong ammonia solution may be used. Under no circumstances whatever should the sulphuric acid be added to the dye-bath, otherwise the colour-acid will be precipitated. In order to preserve uniformity of dye in several lots of material, it is very advisable not to develop different shades of blue in the same acid-bath. The acid-bath should never be employed at a temperature above 80° C., otherwise the blue is less brilliant.

In order to match-off any given shade, a small sample of the woollen material must occasionally be taken from the bulk during the dyeing operation, and passed through warm dilute acid to develop the blue. Only in this way is it possible to regulate what amount of colour solution should be added to the dye-bath, and to determine the duration of the dyeing operation.

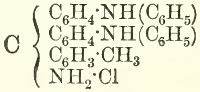
Many Alkali Blues are not improved in colouring power by an addition of carbonate of soda to the dye-bath; they seem to be already sufficiently alkaline, while others give even inferior colours if the addition is made. In all cases a large excess of alkaline salt is to be avoided, since it tends to impoverish the colour.

Colours said to be somewhat faster to milling are obtained by adding zinc sulphate or alum to the acid-bath, since these salts form insoluble lakes with the colouring matter.

Alkali Blue may be employed for the purpose of obtaining compound colours, by using it in conjunction with various acid-colours, *e.g.*, Croceïn Scarlet or Orange, &c. In these cases the acid bath is dispensed with, and after dyeing with Alkali Blue and washing, the wool is at once worked in the dye-bath of the acid-colour, with the necessary additions. The development of the blue, and the dyeing of the scarlet, orange, &c., thus take place simultaneously.

Application to Silk.—Silk is dyed like wool, but it is preferable to use borax in the dye-bath instead of carbonate of soda or ammonia.

321. Rosaniline Violets.



$$C\left\{\begin{array}{l} C_6H_4\cdot NH(C_6H_5)\\ C_6H_4\cdot NH(C_6H_5)\\ C_6H_3\cdot CH_3\\ NH_2\cdot Cl\end{array}\right.$$

These violets, also called by such names as Phenyl Violet, Spirit Violet, Parma Violet, Imperial Violet, &c., are hydrochlorides of mono- and di-phenyl-rosaniline. They find now only a limited use, being less bright than the Methyl Violets; they are, however, said to be somewhat faster to light and to milling, and may be used with advantage when a dull, moderately-fast violet is required, *e.g.*, in felt-hat dyeing.

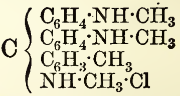
Closely related to Rosaniline Violet is the so-called Regina Purple (Brook, Simpson, and Spiller).

Application to Cotton.—Prepare the cotton with tannic acid and tartar emetic, and dye in a bath slightly acidulated with sulphuric acid or alum.

Application to Wool.—Dye at 60°—80° C. in a colour solution acidulated with 4 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). Since these are basic colouring matters, the need of acidulating the bath is noteworthy.

Application to Silk.—Dye at 60°—80° C. in a bath containing boiled-off liquor, slightly acidulated with sulphuric acid.

322. Hofmann's Violet.



$$C\left\{\begin{array}{l}C_6H_4\cdot NH\cdot CH_3\\ C_6H_4\cdot NH\cdot CH_3\\ C_6H_3\cdot CH_3\\ NH\cdot CH_3\cdot Cl\end{array}\right.$$

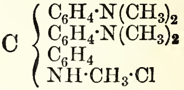
This colouring matter, also called Dahlia, Primula, &c., is considered as the hydrochloride of the base trimethylrosaniline; it is only used for red shades of violet, the bluish violets being better obtained from the Methyl Violets. The colour it yields is not fast to light.

Application to Cotton.—Prepare the cotton with tannic acid and tartar emetic, or with sulphated oil and aluminium acetate; wash and dye at 45°—50° C. in a neutral bath.

Application to Wool.—Dye at 60°—80° C. in a neutral bath, or with the addition of 2—4 per cent. of soap.

Application to Silk.—Dye at 50°—60° C. in a bath containing soap or "boiled-off" liquor, with or without the addition of a little sulphuric acid. Wash and brighten in a bath slightly acidulated with acetic or tartaric acid.

323. Methyl Violet.



$$C\left\{\begin{array}{l}C_6H_4\cdot N(CH_3)_2\\ C_6H_4\cdot N(CH_3)_2\\ C_6H_4\\ NH\cdot CH_3\cdot Cl\end{array}\right.$$

This colouring matter, also called Paris Violet, is considered as the hydrochloride of penta-methyl-para-rosaniline. Various brands are sold—*e.g.*, Methyl Violet R, B, 3 B, &c.—according as they yield red or blue shades of violet.

Some of the Methyl Violets are zinc double salts, and are then sold in the crystalline state; with these the addition of soap to the dye-bath must be strictly avoided.

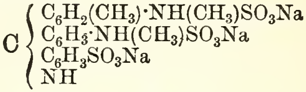
The methods of applying them to the textile fibres are identical with those employed for Hofmann's Violet.

324. Benzylrosaniline Violet.—This colouring matter is the benzyl (C_7H_7) derivative of Methyl Violet. The most highly benzylated product is generally sold as Methyl Violet 6B, and by mixing this in different proportions with Methyl Violet B, the various marks of Methyl Violet 2B, 3B, 4B, 5B are obtained.

Benzyl Violet yields much bluer shades of violet than Methyl Violet, although the method of its application to the various fibres is very similar. It bears the addition of a little sulphuric acid to the dye-bath better than Methyl Violet.

Alkali Violet (Meister, Lucius, & Brüning) is applied in the same manner as Alkali Blue.

325. Acid Violet 4 RS. (BASF).



$$C\left\{\begin{array}{l} C_6H_2(CH_3)\cdot NH(CH_3)SO_3Na \\ C_6H_3\cdot NH(CH_3)SO_3Na \\ C_6H_3SO_3Na \\ NH \end{array}\right.$$

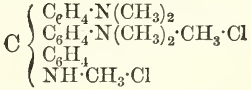
This colouring matter is the sodium salt of di-methyl-rosaniline-tri-sulphonic acid.

Acid Violet 5 RS (BASF) is the corresponding monomethyl compound.

Acid Violet 6 B (BASF) is the corresponding benzyl-methyl compound.

These colouring matters, sold by several manufacturers with different brands, are adapted only for wool and silk, and are applied in the same manner as Acid Magenta. They are useful, in conjunction with other acid colouring matters, for producing compound shades.

326. Methyl Green.



$$C\left\{\begin{array}{l} C_6H_4\cdot N(CH_3)_2 \\ C_6H_4\cdot N(CH_3)_2\cdot CH_3\cdot Cl \\ C_6H_4 \\ NH\cdot CH_3\cdot Cl \end{array}\right.$$

This colouring matter may be regarded as the methyl chloride compound of Methyl Violet. It occurs in commerce in the crystalline state as a zinc double salt.

Although still used, it has been very largely supplanted by the Acid and Benzaldehyde Greens, since these are much cheaper, and offer certain advantages in point of application and stability.

Application to Cotton.—Dye in the same manner as with Benzaldehyde Green.

Application to Wool.—Owing to the weak attraction which wool has for Methyl Green, it is necessary that it should be mordanted previous to being dyed with this colouring matter. The ordinary mordants, however, are of no use, and recourse is had to the singular and strong affinity which amorphous sulphur has for Methyl Green.

The wool is mordanted in a bath containing 10—20 per cent. of thiosulphate of soda (usually called hyposulphite of soda) and acidified with 5—10 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), or hydrochloric acid, 32° Tw. (Sp. Gr. 1·16). Introduce the wool into the milky liquid at 40° C., raise the temperature gradually to 80° C. in the course of an hour, then wash well. Dye at 50°—60° C. in a separate bath containing Methyl Green and 2—4 per cent. of borax or acetate of soda.

The addition of these latter salts to the dye-bath has the effect of neutralising the acid remaining in the wool after washing; if, however, previous to dyeing, the wool is worked for about a quarter of an hour at 70° C. in a weak solution of carbonate of soda or ammonia, their addition to the dye-bath is unnecessary.

The shade produced by Methyl Green is always bluish, and if the temperature of the dye-bath is raised to 100° C. it becomes still bluer, owing to a portion of the colouring matter decomposing at this temperature with elimination of methyl chloride and the production of Methyl Violet; the effect obtained is that of a mixture of green and violet, namely, blue (*Peacock blue*). If it is desired to obtain yellower shades of green, Picric Acid may be added to the dye-bath, but since this only dyes in an acid-bath (a condition which is prejudicial to the dyeing property of Methyl Green) one must add also a small proportion of acetate of zinc. This salt is gradually decomposed by the sulphur already fixed on the wool, and the liberated acetic acid causes the Picric Acid to dye, while it does not prevent the Methyl Green from doing so. The zinc sulphide produced, acts as a mordant for the Methyl Green in the same manner as the sulphur. Should, however, the Methyl Green dye slowly, from over-acidity of the bath, the addition of a little acetate of soda is necessary.

It is essential that in the operations of mordanting and dyeing, the use of metal, either in the dye-vessels themselves or in the utensils employed, should be strictly avoided, otherwise the wool may acquire a dark colour, or be spotted, by the production of metallic sulphides.

Application to Silk.—Dye exactly as in the case of Benzaldehyde Green.

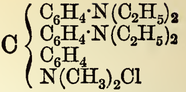
327. **Auramine** (BASF) (Soc. of Chem. Ind., Basle). $[C_6H_4N(CH_3)_2]_2 \cdot C \cdot NH \cdot HCl$.—This yellow colouring matter is the hydrochloride of tetra-methyl-diamido-benzo-phenon-imide. It is particularly useful to the cotton-dyer, and is said to resist the action of light and soap solutions fairly well, but is readily affected by chlorine. It should be dissolved in hot water, but the solution should not be boiled, since the colouring matter is thereby decomposed. It is useful for producing compound shades in conjunction with other basic colouring matters, *e.g.*, Safranine, Benzaldehyde Green, etc.

Application to Cotton.—Mordant the cotton with tannic acid and tartar emetic, and dye in a separate bath. Introduce the cotton into the cold colour solution, and raise the temperature of the bath to 40°—50° C.

Application to Wool.—Dye in a neutral bath. Enter cold and heat gradually to 70° C. Better colours are said to be obtained if the wool is previously mordanted with sulphur, after the manner in vogue for Methyl Green.

Application to Silk.—Dye in the same manner as with Magenta.

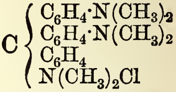
328. Ethyl Purple 6 B (BASF).



$$C\left\{\begin{array}{l}C_6H_4{\cdot}N(C_2H_5)_2\\C_6H_4{\cdot}N(C_2H_5)_2\\C_6H_4\\N(CH_3)_2Cl\end{array}\right.$$

This colouring matter is the hydrochloride of hexa-ethyl-para-rosaniline. It is the bluest shade of violet at present known, and is applied to the various fibres in the same way as Hofmann's Violet.

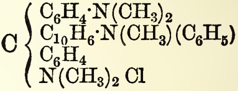
329. Crystal Violet 5 BO (BASF).



$$C\left\{\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_6H_4{\cdot}N(CH_3)_2\\C_6H_4\\N(CH_3)_2Cl\end{array}\right.$$

This colouring matter is the hydrochloride of hexa-methyl-para-rosaniline. It is applied to various fibres like Hofmann's Violet, over which it possesses the advantage of greater colouring power, of extreme solubility in water, and of having no tendency to produce a bronze scum on the surface of the dye liquor or on the dyed material.

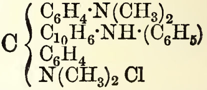
330. Victoria Blue 4 R (BASF).



$$C\left\{\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_{10}H_6{\cdot}N(CH_3)(C_6H_5)\\C_6H_4\\N(CH_3)_2\,Cl\end{array}\right.$$

This colouring matter is the hydrochloride of penta-methyl-phenyl-triamido-diphenyl-α-naphthyl-carbinol. It is applied to the various fibres in the same manner as Hofmann's Violet. Wool and silk may be dyed with the addition of a little acetic or sulphuric acid to the bath, in the same manner as acid colours. The dyeing power is thereby somewhat lessened and the bath is not so well exhausted, but the colour obtained seems brighter.

331. Victoria Blue B (BASF).



$$C\left\{\begin{array}{l}C_6H_4{\cdot}N(CH_3)_2\\C_{10}H_6{\cdot}NH{\cdot}(C_6H_5)\\C_6H_4\\N(CH_3)_2\,Cl\end{array}\right.$$

This is the tetra-methyl compound corresponding to Victoria Blue 4 R, and may be applied in the same way.

332. Night Blue (BASF). This colouring matter is closely related to the last, and is applied to the textile fibres in a similar manner. It requires to be dissolved in dilute acetic acid to prevent decomposition on boiling.

333. Phosphine [$C_{20}H_{17}N_3 \cdot HCl$]. —This orange colouring matter (said to be a quinoline derivative) is the hydrochloride of the base chrysaniline. Its dyeing properties are similar to those of Magenta, and it is applied to the textile fibres in the same manner.

It finds only a limited use in wool- and silk-dyeing because of its expense.

334. Rosolane [$C_{27}H_{24}N_9 \cdot HCl$].—This colouring matter is the hydrochloride of the base mauveïne; it is, indeed, the original Perkin's Violet. It is sold at the present time in the form of a paste.

Its method of application is similar to that of the Methyl Violets. Although itself not requiring a mordant, it may be used in conjunction with polygenetic colouring matters for the production of compound shades. It is used as a substitute for Orchil or Ammoniacal Cochineal in the production of bright greys.

b. Induline and Safranine Group.

335. Indulines.—These comprise a number of colouring matters made by different processes, but all possessing somewhat similar dyeing properties. They are known by a variety of commercial names, *e.g.*, Violaniline, Nigrosine, Elberfeld Blue, Bengaline, Aniline Grey, Coupier's Blue, Roubaix Blue, &c.

Those used for cotton-dyeing are insoluble in water, and require to be dissolved in methylated spirit. These Spirit Indulines are hydrochlorides of a colour-base, *e.g.*, violaniline, triphenyl-violaniline, &c. For wool- and silk-dyeing they are treated with strong sulphuric acid; they are thus rendered soluble in water, and are sold as sodium salts of the corresponding sulphonic acids.

They all yield dark dull blue colours, not unlike indigo-vat blues, to imitate which they are frequently employed.

Application to Cotton.—Prepare the cotton with tannic acid and tartar emetic, wash, and dye in a separate bath containing the colour solution, acidified slightly with sulphuric acid or by the addition of alum (10 per cent.). Dye at a temperature of about 60° C. The bath is not exhausted, and must be preserved for succeeding lots of material. One may also employ the indigo-vat method.

Application to Wool.—Owing to the precipitation of the free sulphonic acids of these colours on the addition of acid to their solutions, it is extremely difficult to dye light shades evenly with them. They are best adapted for dyeing dark shades.

Add the requisite amount of colour-solution (5—15 per cent.) to the dye-bath, heat to 100° C. as rapidly as possible, enter the wool, and boil 1—1½ hour, without any other addition. Continue now to boil one hour longer, during which period add from time to time dilute sulphuric acid in small portions. Use 5—15 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), according to the amount of colouring matter employed.

The long boiling with colour solution alone, enables the wool to become thoroughly permeated with the colouring matter while still in the soluble state. An addition of 5—10 per cent. of borax, carbonate of soda, or strong ammonia solution at this stage is beneficial. The actual dyeing of the wool begins only when the bath is acidulated; the addition of acid should always be made slowly, so that the wool may take up the gradually precipitated colouring matter as evenly as possible.

Wool is said to dye much better with Induline if it has been previously rinsed in a weak solution of bleaching-powder and then in dilute hydrochloric acid.

These colours have been frequently recommended as good substitutes for indigo-vat blues. Although fairly fast to light, they gradually lose their bluish tint and brilliancy on exposure, and assume a dull greyish tone. Towards weak alkalis they are moderately fast; the action of acids they withstand perfectly In conjunction with other acid-colours they are useful for producing a large variety of compound shades.

Application to Silk.—Dye in a bath containing "boiled-off" liquor, acidified slightly with sulphuric acid. Enter the silk at 60° C., add the colour solution gradually, raise the temperature gradually to 100° C., and boil half an hour. Wash and brighten with dilute sulphuric acid.

336. **Naphthalene Pink** [$C_{30}H_{21}N_3 \cdot HCl + H_2O$].—This colouring matter, also called Magdala Red, and derived from amido-azo-naphthalene, is the hydrochloride of the base rosa-naphthylamine. It is but little used, namely, for the purpose of obtaining on silk bright pinks, which have a strong yellowish-red fluorescence.

Application to Silk—Dye in a bath containing "boiled-off" liquor, with or without the addition of sulphuric acid. Brighten with dilute sulphuric or tartaric acid. The colour is faster than that given by Magenta, Eosin, or Safranine; it is fast to dilute acids and alkalis, but not to light.

337. **Safranine** [$C_{21}H_{22}N_4 \cdot HCl$].—In chemical constitution this red colouring matter is apparently allied to Magenta, and is the hydrochloride of a colour-base safranine. It is applied to the various fibres in the same manner as Magenta. On wool the colour is not fast to light. Strictly speaking, the name Safranine is given to several closely-allied products. *Fuchsia* (Soc. Ch. Ind., Basle) is dimethyl-aniline-safranine.

Application to Cotton.—Prepare the cotton with tannic acid and tartar emetic, wash and dye in a neutral bath at 50° C. One may also steep the cotton in a solution of lead acetate (with or without previous impregnation with a solution of soap), dry, and dye in a neutral bath of the colouring matter; the colour thus obtained is objectionable because of the lead it contains. Fixed with tannic acid and tartar emetic the colour is fairly fast to light.

Application to Wool and Silk.—Dye in the same manner as with Magenta.

Neutral Red—(L. Cassella & Co.).—This colouring matter and others called *Neutral Blue* and *Neutral Violet* being allied to Safranine, are all applied to the various textile fibres by similar methods. They yield dull shades of red, blue, and violet respectively, not fast to light on wool. They are of little use in wool- and silk-dyeing, but may be used with advantage by the cotton-dyer for producing compound shades.

New Blue D (L. Cassella & Co.).—This colouring matter gives a colour closely resembling that of vat-indigo blue, which on cotton is extremely fast to light. Although affected by alkalis it is well adapted for cotton-dyeing, and may in many cases replace vat-indigo blue. New Blue D is frequently used in conjunction with Methylene Blue or other basic colouring matters.

Application to Cotton.—Mordant the cotton with tannic acid and tartar emetic, and dye in a neutral bath of the colour solution.

(c) *Aniline Black Group.*

338. Aniline Black.—Unlike other colouring matters, Aniline Black is not a commercial article. For the purpose of the dyer it must be produced upon the fibre itself. Little or nothing is known of its chemical constitution. It is a product of the oxidation of a salt of aniline, generally aniline hydrochloride, and appears to exist in two states of oxidation. The less oxidised product is a blue-black, somewhat sensitive to the action of acids, particularly sulphurous acid, under the influence of which it acquires a greenish tint. The original colour can only be temporarily restored by treatment with an alkaline solution. The more highly oxidised product is a violet-toned black, which is not turned green by acids. This is produced by submitting the former to a supplementary oxidation. It is remarkable for its extreme fastness to acids, alkalis, light, &c., and is indeed one of the most permanent dyes known.

339. *Application to Cotton.*—For dyeing cotton Aniline Black the most usual oxidising agent employed is bichromate of potash, or chromic acid. According to the temperature at which the dyeing is effected, two methods may be distinguished, namely, the *warm method* and the *cold method.*

Warm Method. — For 100 kilos. of cotton the dye-bath contains the following ingredients: 1,600 litres of water, 40 kilos. of hydrochloric acid 34° Tw. (Sp. Gr. 1·17), 10 kilos. of aniline, 10—14 kilos. of bichromate of potash.

These proportions may be varied according to the particular shade of black required. A portion of the hydrochloric acid may also be replaced by an equivalent amount of sulphuric acid. Use, for example, 24 kilos. of hydrochloric acid, and 4—6 kilos. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). The intensity of the colour, however, is always regulated by the amount of aniline employed.

The aniline and hydrochloric acid diluted slightly with water, are carefully mixed in a suitable glazed earthenware vessel, and the acid solution of aniline hydrochloride thus obtained is added to the dye-bath previously filled with cold water. The bichromate of potash is dissolved separately in a little warm water and added to the bath.

The cotton is worked for an hour in the cold solution, until, indeed, it has acquired a considerable intensity of colour, after which the temperature is gradually raised to 50°—60° C. The whole operation may last from 1—3 hours.

Another method is as follows: Dye the cotton in the cold for one hour with only half the quantity of the several ingredients added to the bath, then add the remainder, and continue the dyeing in the cold for an hour longer; after this raise the temperature gradually to 50°—60° C., and continue the dyeing for another hour.

The more concentrated the solution, and the greater its acidity, the more rapidly does the dyeing take place. Excess of acid and prolonged heating tend to give bronze-coloured blacks, and much of the colouring matter is only superficially fixed. If, however, the heating has been of short duration, the black has a bluish tone, and is liable to become green under the influence of acids.

It is essential that the temperature of the bath should be raised very gradually, otherwise there is a great loss of colouring matter, since much of it is then precipitated in the bath and not on the fibre.

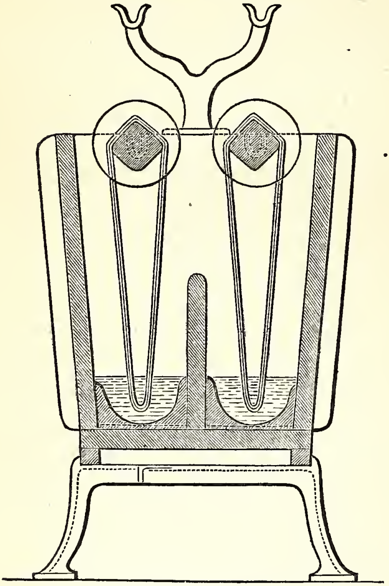


Fig. 85.—Aniline Black Dyeing Machine.

After dyeing, the cotton must be well washed with water, then boiled in a solution of soap containing 5—10 grams per litre, with or without the addition of a little carbonate of soda, and finally dried.

340. Cold Method. — According to this method the dyeing operation is conducted entirely in the cold, the proportions of the ingredients and the concentration of the bath being altered to render this possible.

For 100 kilograms of cotton use 16—20 kilograms of hydrochloric acid, 20 kilograms of sulphuric acid, 8—10 kilograms of aniline, 14—20 kilograms of bichromate of potash, 10 kilograms of ferrous sulphate. The quantity of water should be very much smaller than in the warm method, otherwise the dyeing would either be incomplete, or would take too long. Fig. 85 represents an apparatus of MM. Tulpin frerès for dyeing cotton yarn

Aniline Black. It is specially designed so that the hanks can be properly manipulated in as little liquid as possible. It consists of a strong wooden dye-bath, about two metres long, and longitudinally divided into two compartments, each with rounded bottom. Above are two corresponding square rollers, each capable of holding about five kilograms of cotton yarn; there is also a support with two arms, on which the rollers can be placed either at the end of the dyeing process or for the purpose of filling them with yarn before beginning. Several such dye-baths are arranged in line, the rollers being turned by power, alternately to right and left, in order to avoid entanglement of the hanks. The use of such a machine saves labour, prevents the corrosion of the workmen's hands by the chromic acid, and gives a more regularly oxidised black.

It will be noticed that the proportions of bichromate of potash and acid employed in the cold method are larger than in the warm method; this is in order to facilitate the oxidation of the aniline salt at the lower temperature. The addition of the sulphuric acid has a similar effect, but it also tends to yield ultimately a more pleasing tone of black. The use of hydrochloric acid produces blue-blacks, while sulphuric acid alone gives such as are of a reddish hue. The addition of the ferrous sulphate is for the purpose of rendering the black less liable to turn green; of course in the bath it is changed to ferric sulphate, and this acts as an oxidising agent.

The method of preparing the dye-bath for the cold method is similar to that already described. The aniline hydrochloride is previously made by mixing the aniline and hydrochloric acid; separate solutions of the ferrous sulphate, bichromate of potash, and sulphuric acid are also kept in readiness. The cotton is first worked for about an hour with only half the full amount of the several ingredients in the bath. At the end of this time, when the cotton has already acquired quite a black colour, it is lifted out, the other half of the ingredients is added, the cotton is then re-entered, and the dyeing is continued 1—1½ hour longer.

After dyeing, the cotton is well washed and boiled with a solution of soap and carbonate of soda, as previously stated, and dried. The use of soap alone gives violet-toned blacks; the addition of carbonate of soda makes the shade bluer.

Although the black produced by either of the above methods, but especially by the cold method, is tolerably stable, it is necessary, in order to render it perfectly ungreenable, to submit the dyed cotton, after washing, to a supplementary oxidation. Several methods have been proposed for this purpose, but perhaps the following, in which ferric sulphate is the oxidising agent, is the most serviceable: Prepare a mixture of 20 kilograms of ferrous sulphate, 5 kilograms of bichromate of potash, 15—18 litres of sulphuric acid 168° Tw., 60—70 litres of water. Add 5 litres of this mixture to 500 litres of water, and work the cotton in the solution for three-quarters of an hour at 75°C.; then wash well, boil with soap, and dry.

Another method, depending for its efficacy upon the optical effect that a mixture of violet and green appears blue, is to dye the black in a weak solution of Methyl Violet. This violet is fixed, it is supposed, by reason of the cotton itself having been partially oxidised and changed into oxycellulose during the dyeing process.

Two other methods of producing Aniline Black on cotton, though not practically employed, possess sufficient interest to deserve mention. One is that borrowed from the method so successful in the printing of calico with Aniline Black. It is based upon oxidising the aniline salt by means of potassium chlorate in the presence of vanadium. The cotton is impregnated with a somewhat concentrated solution containing 5—20 per cent. of aniline hydrochloride (according to the intensity and fastness of the black required), 2—10 per cent. of potassium chlorate, and a very minute quantity of vanadium chloride (not more than $\frac{1}{300}$ of the weight of aniline hydrochloride employed). After wringing out the excess of liquid, the colour is developed by hanging the cotton in an ageing stove heated to 25°—30° C., and in which the air is kept slightly moist by admitting a little steam. The chief defect of this process is that an uneven colour is liable to be produced, since the oxidation will take place unequally if there is a partial drying of the fibres, or an unequal exposure of the fibres to the air.

The other method referred to is that proposed by Goppelsroeder, in which a vat of reduced Aniline Black is made, the cotton being then dyed in it just as in an indigo-vat.

The Aniline Black is first prepared separately, namely, by heating a solution containing aniline hydrochloride, potassium chlorate, ammonium chloride, and copper sulphate. The black pigment thus produced is purified by boiling with water, and afterwards with alcohol. It is then heated with a solution of caustic potash, and the colour-base of the black thus liberated is washed, dried, and dissolved in fuming sulphuric acid. This solution is poured into cold water, and the greenish-black precipitate thus produced is dissolved in caustic alkali, and reduced by heating with the addition of glucose, hydrosulphite of soda, or zinc powder. Ferrous sulphate and lime are inoperative. If cotton be steeped in the brownish-yellow solution thus obtained, and then exposed to the air, it acquires gradually a blue colour. By submitting this colour to a supplementary oxidation (*see* p. 394) it changes to a light grey or deep black, according to the concentration of the vat. A judicious combination of the aniline black vat with an indigo-vat may yield very fast deep blues.

On account of its great fastness, Aniline Black is extremely serviceable for dyeing unspun cotton, intended to be mixed with loose wool previous to spinning; it may also be associated with Logwood black, since chromic oxide is precipitated on the fibre along with the Aniline Black, in sufficient quantity to serve as a mordant for dyeing subsequently in a Logwood bath. If necessary, an additional saddening with acetate of iron may also take place.

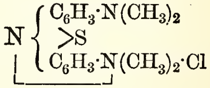
341. *Application to Wool and Silk.*—At the present time these fibres, especially the former, cannot be dyed satisfactorily with Aniline Black. It would appear as if the reducing action of the fibres themselves hindered the oxidation of the aniline salt. Better results are said to be obtained if the fibres are previously oxidised by immersing them for some time either in a weak solution of permanganate of potash, or in a dilute solution of bleaching powder to which hydrochloric acid has been added. After this preliminary process, the wool or silk is washed and dyed by a process exactly analogous to the one described for dyeing cotton.

342. **Naphthylamine Violet.**—This colouring matter, derived from naphthylamine hydrochloride in a manner similar to that by which Aniline Black is obtained, must also be produced upon the fibre itself. It gives a dull greyish- or brownish-violet on cotton, which is not quite so fast as Aniline Black. It does not appear to be used in practice by the dyer. Reference has already been made to the dyeing of manganese-brown cotton with naphthylamine salt (*see* p. 226).

(*d*) *Aniline Colours containing Sulphur.*

343. **Aldehyde Green** [$C_{22}H_{27}N_3S_2O$].—This colouring matter, now seldom used, is invariably prepared by the dyer himself, by the action of aldehyde upon a solution of Magenta dissolved in strong sulphuric acid; the blue solution thus obtained is then poured into a boiling solution of thiosulphate of soda. The acid solution is filtered, and should be at once used for dyeing silk or wool, since it decomposes on long standing. It is not applicable to cotton.

344. **Methylene Blue.**



$$N\left\{\begin{matrix} C_6H_3\cdot N(CH_3)_2 \\ >S \\ C_6H_3\cdot N(CH_3)_2\cdot Cl \end{matrix}\right.$$

Methylene Blue, a derivative of dimethyl-aniline, is sold as a zinc double salt in the form of powder. It is principally used in cotton-dyeing, and gives a greenish blue, much valued on account of its great fastness to soap and also, it is said, to light. For silk- and wool-dyeing it has less importance; since on these fibres it is not fast to light nor is it so bright as other blues.

Application to Cotton.—The cotton is prepared with tannic acid and tartar emetic, then washed and dyed in a separate bath containing Methylene Blue solution. The addition to the dye-bath of a small quantity of carbonate of soda or ammonia is beneficial. Enter the cotton cold, and raise the temperature gradually to 100° C.

For dark indigo-blue shades the tartar emetic may be substituted by nitrate of iron.

Application to Wool.—Add to the dye-bath the requisite amount of colour in solution (0·5—5 per cent.) and 1—2 per cent. of carbonate of soda (crystals) or ammonia. Enter the wool cold, and raise the temperature gradually to 100° C. in the course of half an hour, and boil half an hour longer. The dye-bath cannot be exhausted. Excess of sodium carbonate is injurious.

Ethylene Blue.—This colouring matter is applied like Methylene Blue, and has similar properties. It is prepared from diethyl-aniline.

CHAPTER XVII.

QUINOLINE COLOURING MATTERS.

345. Flavaniline (Meister, Lucius, and Brüning)

$[C_9H_5N(CH_3)\cdot C_6H_4(NH_2)\cdot HCl]$.

This basic yellow colouring matter, derived from acetanilide, is the hydrochloride of the quinoline base flavaniline. It is applied to cotton, wool, and silk, in the same manner as Magenta. On wool the colour is developed a little by passing the dyed material through dilute sulphuric acid. Brighter colours are obtained on wool mordanted with thiosulphate of soda according to the method employed when dyeing with Methyl Green. Flavaniline yellow is not fast to light.

Flavaniline S is an alkali salt of the sulphonic acid of the flavaniline base. It is applied to wool and silk in an acid bath.

Quinoline Blue [$C_{28}H_{35}N_2I$].—This disused colouring matter, also called Cyanine, is applied to cotton, wool, and silk in the same manner as Magenta. The colours it yields are very fugitive towards light.

Quinoline Yellow (Act. Gesell. Farben Fabrik, Berlin).—This colouring matter is the sodium salt of the sulphonic acid of quinoline-phthaleïn. It gives a pure yellow colour, and is applied in an acid dye-bath in the same manner as other sulphonic acid colouring matters.

CHAPTER XVIII.

PHENOL COLOURING MATTERS.

(*a*) *Nitro Compounds.*

346. Picric Acid [$C_6H_2(NO_2)_3{\cdot}OH$].—This colouring matter is tri-nitro-phenol; it is used only in silk- and wool-dyeing. Cotton has no attraction for it, and although it may be fixed on this fibre by means of albumen, the method has no practical value. The animal fibres, on the contrary, readily take up Picric Acid from an acid solution.

It gives a clear bright yellow, free from any tinge of orange; indeed, when compared with most other yellows it appears to have a greenish hue.

Application to Wool. — Dye for ½—1 hour at 60°—100° C. with 1—4 per cent. of Picric Acid, with the addition of 2—4 per cent. of sulphuric acid, 168° Tw.

(Sp. Gr. 1·84). The bath must be preserved, since it cannot be exhausted.

By repeated washing with water only, it is possible to remove nearly the whole of the colour from the dyed fibre. It does not stand milling well, both on this account and because the colour becomes brownish under the influence of alkalis.

It is also not a good dye for the woollen part of mixed goods (wool and cotton), since it comes off in the tannin bath used for preparing the cotton. It is frequently employed for the production of compound colours, *e.g.*, with Methyl Green and with Indigo Carmine for yellowish greens, with Acid Violet for olive, &c.

A noteworthy feature of Picric Acid yellow is that on exposure to light it rapidly becomes darker, acquiring a dull orange colour, which does not readily fade.

Application to Silk.—Dye with 0·5—1 per cent. of Picric Acid in a bath slightly acidified with sulphuric acid, with or without the addition of "boiled-off" liquor. The colour marks off on paper, if submitted to pressure for some time. The compound colours dyed with Picric Acid and Methyl Violet are fluorescent.

The method of dyeing a weighted yellow on silk by first preparing the fibre with lead acetate, and then dyeing with Picric Acid, is not to be recommended, since the colour blackens in the presence of sulphuretted hydrogen, and the picrate of lead causes the silk, when ignited, to burn like touch-paper.

347. **Phenyl Brown.**—This colouring matter, which consists of a mixture of dinitrophenol $C_6H_3(NO_2)_2{\cdot}OH$ with an amorphous brown substance, is not now used in dyeing to any very large extent. It is not applicable to cotton.

Application to Wool.—It gives nice brown shades, which are said to be very fast to light.

Dye in a bath slightly acidified with sulphuric acid. If the wool is boiled with bichromate of potash after dyeing, the colour assumes a redder tone.

Application to Silk.—Dye in a bath slightly acidified with sulphuric acid.

348. Victoria Yellow [$C_6H_2(CH_3)(NO_2)_2{\cdot}OK$].—This colouring matter is the potassium salt of dinitro-*p*-cresol. The dyes it yields are so very fugitive that it is now no longer employed.

It is applied to wool and silk in the same way as Picric Acid.

349. Campobello Yellow [$C_{10}H_6(NO_2){\cdot}ONa$].—This colouring matter is the sodium salt of *a*-nitro-*a*-naphthol; it was formerly also sold as French Yellow and Chryseïnic Acid. It is applied in the same way as Naphthol Yellow, and gives similar shades.

It is applicable only to silk and wool, but the colour is neither fast to light nor to washing.

350. Naphthol Yellow [$C_{10}H_5(NO_2)_2{\cdot}ONa + H_2O$].—This colouring matter is the sodium or calcium salt of dinitro-*a*-naphthol; it is also known by the following names: Martius Yellow, Manchester Yellow, Golden Yellow, Saffron Yellow, Primrose, Naphthaline Yellow, &c.

It is applicable only to silk and wool, but, since it is volatile even at low temperatures, it has the defect of marking off.

Application to Wool.—Dye in an acid bath for 1 hour with 0·5—3 per cent. of colouring matter and 3—6 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). Enter the wool at 40° C., and heat gradually to 100° C. If desirable, one may also acidify with 5—10 per cent. of alum instead of sulphuric acid. According to the amount of colouring matter employed, the colour varies from a pale lemon-yellow to a deep and brilliant orange-yellow. It is not fast to light, and is not suitable for goods which have to be milled.

Application to Silk.—It is applied in the same manner as Picric Acid.

351. Naphthol Yellow S (BASF).

$$[C_{10}H_4{\cdot}(NO_2)_2{\cdot}ONa{\cdot}SO_3Na]$$

This colouring matter is the sodium salt of the sulphonic acid of Naphthol Yellow; it is used only in silk- and wool-dyeing. It is very much faster to washing than either Picric Acid or Naphthol Yellow. It is not volatile on steaming, and does not mark off, but is fugitive to light. It is applied in the same way as Naphthol Yellow.

352. New Yellow (F. Baeyer & Co.)

$$[C_{10}H_5 \cdot NO_2 \cdot OK \cdot SO_3K]$$

is the potassium salt of the nitro derivative of β-naphthol-α-monosulphonic acid.

Application to Wool.—The method of dyeing is the same as with Naphthol Yellow, and similar shades are produced. The colour is not fast to light. The addition of a small percentage of stannic chloride to the dye-bath adds brilliancy to the colour.

Application to Silk.—Dye in a bath slightly acidified with sulphuric acid, and without the addition of "boiled-off" liquor or soap.

353. Palatine Orange (BASF), $[C_{12}H_4(NO_2)_4(ONH_4)_2]$.—This colouring matter is the ammonium salt of tetra-nitro-γ-diphenol. It is applied to wool and silk in a bath acidulated with sulphuric or acetic acid.

354. Heliochrysin $[C_{10}H_3(NO_2)_4ONa]$.—This colouring matter is the sodium salt of tetra-nitro-naphthol, it is also known as Sun Gold. It gives fine orange shades on wool and silk, but it is not fast to light, and has scarcely been employed in practice.

355. Aurantia $[N(C_6H_2(NO_2)_3)_2NH_4]$.—This orange colouring matter is the ammonium salt of hexa-nitro-diphenyl-amine; it is also known as Imperial Yellow, and is only applicable to wool and silk.

Dye in a bath very slightly acidified with sulphuric acid. Contact of the solution with metallic surfaces must be avoided, since these render the solution brown. Only glass or wooden vessels should be employed for dissolving or dyeing.

It has been stated that Aurantia has decidedly poisonous properties, and occasions skin eruptions, but opinion still seems to be divided on this point.

356. Quite recently C. Lowe has introduced a new blue and a yellow dye, termed respectively Azuro- and Auro-phenylene, which are said to yield colours fast to light and soap. Both are derived from the disused blue colouring matter Azulin. Auro-phenylene is a nitro-derivative.

(*b*) *Colouring Matters produced by the Action of Nitrous Acid on Phenols.*

357. Resorcin Blue [$C_{18}H_3(NH_4)Br_6N_2O_5$] (?).—This colouring matter, also known as Fluorescent Blue, is the ammonium salt of hexa-brom-diazo-resorufin. It is applicable to wool and silk only, more particularly the latter.

Silk dyed with this colour is remarkable for its reddish fluorescence, the red colour appearing very prominently by gas-light. It is said to be fast to light, washing, and acids. When used in combination with other colouring matters it gives pleasing shades, all possessing fluorescence.

Application to Silk.—Dye in a bath containing "boiled-off" liquor or soap, and neutralised with acetic acid. Brighten in a cold bath slightly acidified with tartaric or sulphuric acid.

358. Naphthol Green (L. Cassella & Co.)

[$C_{10}H_5O_7SNFe$](?).

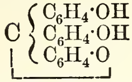
—This colouring matter is the iron compound of nitroso-naphthol-mono-sulphonic acid. It gives an olive-green colour on wool, remarkable for its fastness to light. The colour also bears the action of milling with soap fairly well, but it is much impoverished by the action of carbonate of soda.

Naphthol Green is not applicable in cotton-dyeing.

Application to Wool.—Dye at 100° C. with the addition of 2—3 per cent. of sulphuric acid 168° Tw. (Sp. Gr. 1·04), 20 per cent. of sodium sulphate, and 10 per cent. of ferrous sulphate. It is very useful for producing compound shades in conjunction with other colouring matters which are applied in an acid bath.

(c) *Rosolic Acid Colours.*

359. Aurin.



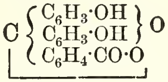
$$C\left\{\begin{matrix} C_6H_4\cdot OH \\ C_6H_4\cdot OH \\ C_6H_4\cdot O \end{matrix}\right.$$

This colouring matter in its commercial form is also called Yellow Corallin.

What is known as Red Corallin or Peony Red is produced from Yellow Corallin by the action of ammonia on it at high temperatures. Owing to the extreme fugitiveness to light, soap, and acids, of the colours they yield, these colouring matters are seldom employed in dyeing. Silk and wool may be dyed in a weak soap bath, heating it gradually to the boiling point; brighten the silk with tartaric acid. They are still used by the calico and woollen printer.

(d) *Phthaleïns.*

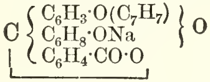
360. Fluoresceïn.



$$C\left\{\begin{matrix} C_6H_3\cdot OH \\ C_6H_3\cdot OH \\ C_6H_4\cdot CO\cdot O \end{matrix}\right. \left.\begin{matrix} \\ \\ \end{matrix}\right\} O$$

Fluoresceïn dyes wool and silk yellow in a slightly acidulated bath; but it is scarcely used in dyeing, because it does not give fast colours, and these are surpassed in beauty of tint by those yielded by other yellow colouring matters. Its sodium compound, known under the name of Uranin, is applied in the same manner.

361. Chrysolin.

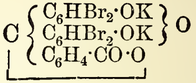


$$C\left\{\begin{matrix} C_6H_3\cdot O(C_7H_7) \\ C_6H_8\cdot ONa \\ C_6H_4\cdot CO\cdot O \end{matrix}\right. \left.\begin{matrix} \\ \\ \end{matrix}\right\} O$$

This colouring matter is the sodium salt of benzylfluoresceïn. It dyes wool and silk in a neutral bath, although a better result is obtained by previously mordanting with alum. The yellow colour produced is similar to that given by Turmeric, but it is said to be faster to light. In cotton-dyeing it may be used for topping Quercitron Bark yellow.

362. Eosins.—There are quite a number of red colouring matters belonging to the class of eosins. They differ from each other both in their composition and the shade they produce.

Eosin J (soluble in water).



$$\mathrm{C}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{C_6HBr_2\cdot OK}\\ \mathrm{C_6HBr_2\cdot OK}\end{array}\right\}\mathrm{O}\\ \mathrm{C_6H_4\cdot CO\cdot O}\end{array}\right.$$

This is the potassium salt of tetra-brom-fluoresceïn. It dyes a yellowish-pink shade.

Eosin B (soluble in water) is an alkali salt of tetra-iodo-fluoresceïn, and dyes a bluish-pink shade. It is also known by the names Erythrosin, Pyrosin B (P. Monnet), and Soluble Primrose (Durand and Huguenin).

Aureosin (Willm, B. & Girard) is a chlorinated fluoresceïn.

Rubeosin (Willm, B. & Girard) is a nitro-chlor-fluoresceïn.

Eosin BN (BASF), also called Safrosin (Soc. Chem. Ind., Basle), is a brom-nitro-fluoresceïn.

Lutécienne (Poirrier) is a mixture of brom-nitro-fluoresceïn, with di- and tetra-nitro-fluoresceïn or Poirrier's Orange 2.

Nopalin and **Imperial Red** contain dinitro-naphthol mixed with brom-nitro-fluoresceïn.

Coccin is a mixture of Aurantia with brom-nitro-fluoresceïn.

Eosin (soluble in alcohol) is the potassium salt of tetra-brom-fluoresceïn-methyl or ethyl ether. It bears also such names as Methyl-eosin, Ethyl-eosin, Primrose (soluble in alcohol), Rose JB, Erythrin, Methyl-erythrin, &c.

The methyl compound gives yellower shades than the ethyl compound. Both give better and brighter shades than the ordinary eosins, which they have largely displaced in silk-dyeing.

Rose Bengal is the sodium salt of tetra-iodo-dichlor-fluoresceïn.

Phloxin (P. Monnet & Co.) is the potassium salt of tetra-brom-dichlor-fluoresceïn.

Cyanosin (P. Monnet & Co.) is the potassium salt of the methyl-ether of Phloxin.

The eosins may be used in cotton-, wool-, or silk-dyeing, and yield bright shades, which vary from yellowish-scarlet to bluish-crimson. The yellowest shade is given by Eosin J or G, then follow Methyl and Ethyl-eosin, Eosin B, Phloxin, and Safrosin. The bluest shade is given by Rose Bengal. Cyanosin, Phloxin, and others are sold, however, in different shades, and are marked accordingly with J, R, or B. Safrosin is not quite so bright on silk as some of the other blue shades, but on wool it gives a good full and bright colour.

The eosins soluble in alcohol give brighter shades than those soluble in water, but, apart from the cost of the alcohol required, they cannot always be used, because the strong yellowish fluorescence which they give is sometimes not desirable.

Application of Eosins to Cotton.—Cotton has naturally no attraction for the eosins, but since they form lakes with metallic oxides (especially protoxides), it is possible to dye this fibre if it is previously mordanted with some metallic salt. The mordants employed are those of zinc and lead. Aluminium salts are also used.

Impregnate the cotton with a cold or tepid solution of sulphated oil, 100 grams per litre; wring out, dry and steam; then work in aluminium acetate at 8° Tw. (Sp. Gr. 1·04) for half an hour, steep 1—2 hours longer, and wring out. Dye in a fresh bath of Eosin solution acidified with 5—10 per cent. of alum. Enter the cotton at 45° C., and allow the bath to cool gradually during the dyeing process.

A strong and hot solution of soap may be substituted for the sulphated oil, and a solution of nitrate acetate or basic acetate of lead at 5° Tw. (Sp. Gr. 1·025) may replace the aluminium acetate. The colours thus obtained have a yellow tone.

Very good bluish shades are produced by impregnating the cotton with the lead solution, then drying and dyeing in Eosin solution.

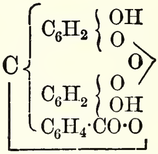
The use of a lead salt has the disadvantage that the colour is blackened if exposed to an atmosphere containing sulphuretted hydrogen. The dye thus obtained is naturally of a poisonous character.

Application to Wool.—Dye with 0·5—2 per cent. of Eosin, with the addition of 5—10 per cent. of alum. Enter the wool at 40° C., and raise the temperature gradually to 100° C. in the course of an hour. If the bath is acidified with acetic or sulphuric acid instead of alum, the shades produced are not so bright, but the wool is less harsh. With Erythrosin the temperature of the dye-bath must be kept below the boiling point.

The water used should be as free from lime as possible, otherwise it causes precipitation and loss of colouring matter. If lime is present, neutralise it with acetic acid before dyeing.

Application to Silk.—Dye in a bath slightly acidified with acetic or sulphuric acid, with or without the addition of "boiled-off" liquor. Wash and brighten with acetic or tartaric acid. Add the colour solution gradually, and heat slowly to 60° C.

363. Galleïn.



$$C\left\{\begin{array}{l} C_6H_2\left\{\begin{array}{l}OH\\ O\end{array}\right. \\ \qquad\quad O \\ C_6H_2\left\{\begin{array}{l}O\\ OH\end{array}\right. \\ C_6H_4\cdot CO\cdot O\end{array}\right.$$

This fine purple colouring matter, sometimes called Anthracene Violet, is derived from phthalic anhydride and pyrogallol. It is sold in the form of a reddish-brown powder or a 10 per cent. paste, not very soluble in cold water, but readily so in hot. It ought to be much more used than it is, since it gives fine purple shades on cotton, wool, and silk, which are tolerably fast both to light and soap.

Application to Cotton.—Prepare the cotton with aluminium, chromium, or iron mordants in the usual manner, and dye in a separate bath with Galleïn. The whole process is identical with that used in dyeing with Alizarin, Logwood, or other polygenetic colouring matters.

All the mordants yield purple colours, those obtained by the use of chromium and iron being bluish, those of tin reddish, and those of aluminium intermediate in tone. All the colours may be regarded as fast to light and soap.

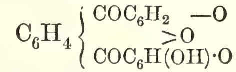
Application to Wool.—Mordant the wool with 2 per cent. of *bichromate of potash.* The addition of sulphuric acid even to the extent of 1 per cent. is injurious, and dulls the colour. Dye in a separate bath with 10—20 per cent. of Galleïn paste, containing 10 per cent. of solid matter. Enter the wool cold, and raise the temperature gradually to the boiling point. The shade thus produced is bluish-purple or violet.

With *aluminium* mordant a much redder and brighter purple is given. Mordant with 6—8 per cent. of aluminium sulphate and 5—7 per cent. of cream of tartar. With the addition of 1—2 per cent. of acetate of lime (solid), the shade is somewhat more intense and slightly brighter. The addition of chalk to the dye-bath is not to be recommended, even with 2 per cent. the colour is much deteriorated. With *iron* mordants Galleïn gives a deep violet colour. Use 8 per cent. ferrous sulphate and 5 per cent. tartar. The single-bath method is also applicable.

All the above Galleïn colours are specially adapted for goods which have to be milled. The chromium mordant is the most generally useful of those mentioned.

Silk is dyed in the same way as with Alizarin (p. 456).

364. Cœruleïn



$$C_6H_4\left\{\begin{array}{l}COC_6H_2\quad -O\\ \qquad\quad >O\\ COC_6H(OH)\cdot O\end{array}\right.$$

This green colouring matter, also called Anthracene Green, is derived from Galleïn by the action of sulphuric acid at a high temperature. It is sold in two forms, either as a thick black paste (Cœruleïn paste) containing

10—20 per cent. of Cœruleïn, or as a black powder. The former is more or less insoluble in water, and requires in some cases the addition of bisulphite of soda to render it soluble. The latter, known as Cœruleïn S, is soluble in water, and is indeed a compound of Cœruleïn with bisulphite of soda [$C_{20}H_8O_6 \cdot 2NaHSO_3$]; this form is the one most easily applied.

At the present time Cœruleïn is mostly employed in calico-printing for producing very fast olive-green shades. The colours it yields both on cotton and on wool are remarkable for their fastness to light, acids, alkalis, &c., and whenever its price permits, it will find an extensive use in the dyeing of these materials. Whatever the mordant used, only different shades of olive-green are obtained. The use of copper dye-vessels should be avoided.

Application to Cotton. — If *insoluble* Cœruleïn is heated with a mixture of caustic alkali (NH_3) and zinc powder, a brownish-red solution of the reduction product *Cœrulin* is obtained, which on exposure to air immediately becomes green again, with precipitation of the original Cœruleïn. This brownish-red liquid or "Cœruleïn-vat" as it might be termed, may be used for dyeing after the manner of the indigo-vat.

If the *soluble* Cœruleïn S is employed, the cotton must be previously prepared with aluminium, chromium, iron, or tin mordant, according to the usual methods, and then dyed in a simple solution of the colouring matter. Care should be taken to begin dyeing at a low temperature, and to raise it very gradually to 100° C. During the dyeing process sulphurous acid is given off, and the liquid becomes green and alkaline. The water employed should be free from salts of lime and other alkaline earths, since these produce insoluble lakes with Cœruleïn. The insoluble form of Cœruleïn may be applied in the same way, if bisulphite of soda is added to the bath to render it soluble, but the results are not quite so satisfactory.

Application to Wool.—On wool the most generally useful mordant is *bichromate of potash.*

Mordant the wool with 2—3 per cent. bichromate of potash and 0—0·7 per cent. sulphuric acid, 168° Tw. (Sp. Gr. 1·84). Without sulphuric acid the colour is slightly paler. Dye in a separate bath containing only Cœruleïn S. Enter the wool cold, and raise the temperature very gradually (say in the course of half an hour) to 60° C. Dye at this temperature for about one hour, then heat gradually in the course of half an hour to 100° C., and boil for a quarter of an hour. The addition to the dye-bath, during the last quarter of an hour, of 1—2 per cent. of chalk, makes the shade bluer, but generally speaking the addition of chalk or calcium acetate to the bath is to be avoided. With 2 per cent. of Cœruleïn S a pale sage-green is obtained, with 5 per cent. a medium olive-green, and with 10 per cent. a very dark green, almost black. These colours may be used instead of indigo-greens, being equally fast to light, milling, &c.

With *aluminium* mordant shades can be obtained which are somewhat bluer or greyer than with bichromate of potash, but they are very apt to be uneven.

With *iron* mordant dirty olive and olive-black shades are obtained. Use 4 per cent. of ferrous sulphate and 8 per cent. of cream of tartar, and dye with 0·5—10 per cent. of Cœruleïn S.

If wool is mordanted with an amount of pure *stannic chloride* equivalent to 5 per cent. $SnCl_2 \cdot 2H_2O$ (tin-crystals), it needs the addition of 40 per cent. of cream of tartar to yield a normal bluish-green colour, when dyed afterwards with 5 per cent. of Cœruleïn S; but it is remarkable that even without the addition of any tartar a full greyish-black colour is obtained. (With the majority of polygenetic colouring matters, stannic chloride is an unsatisfactory mordant.) With 5 per cent. of Cœruleïn S, the colour is perhaps too much like a bad black to be of general use, but with 0·5—2 per cent. very pleasing greys are obtained.

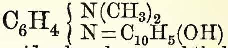
Another method of dyeing with Cœruleïn is to boil the wool with its sodium carbonate solution for some time, and then gradually to acidify with sulphuric acid in order to precipitate the colouring matter within and upon the fibre, but it only yields a dull colour.

By mordanting wool with bichromate of potash and dyeing with mixtures of Cœruleïn S and Alizarin or Anthrapurpurin, a great variety of fast browns and olives are obtained. Cœruleïn S may of course be used in the same bath with all polygenetic colouring matters.

Application to Silk. — Cœruleïn has scarcely been introduced into silk-dyeing, though it is capable of giving good fast shades. Mordant in the usual manner with alum, dye in a separate bath with Cœruleïn S, and brighten with a solution of soap.

(e) *Indophenols.*

365. *α*-Naphthol Blue (L. Cassella & Co.).



$$C_6H_4 \left\{ \begin{array}{l} N(CH_3)_2 \\ N{=}C_{10}H_5(OH) \end{array} \right.$$

Dimethyl-amido-phenyl-oxy-naphthylamine.

—This colouring matter, also called Indophenol Blue N, is produced by oxidising a mixture of dimethyl-*p*-phenylene-diamine and *α*-naphthol, or by the action of nitroso-dimethyl-aniline on *α*-naphthol. It gives colours very similar to vat-indigo blues, and which are said to be moderately fast to light. They are, however, extremely sensitive to the action of acids; even weak acids destroy the blue colour and change it to brown. Indophenol Blue N is better adapted for woollen- and calico-printing than for dyeing.

Under the influence of reducing agents—*e.g.*, glucose and caustic soda, stannous chloride and carbonate of soda, &c.—Indophenol Blue is changed into indophenol-white, which is soluble in pure or acidulated water.

For the preparation of indophenol-white, mix together 10 kilos. of Indophenol Blue (paste) and 60 litres of water; add 30 litres of a 10 per cent. solution of tin crystals ($SnCl_2{\cdot}2H_2O$), and heat to 25° C. until reduction takes place.

Application to Cotton.—Dye for ten minutes at 40° C. in a solution containing 5—10 grams. of indophenol-white per litre, then wring out and wash, and develop the colour by working the cotton for about two minutes at 50° C. in a dilute solution of bichromate of potash. Better colours are obtained if the cotton is previously prepared with sulphated oil.

Application to Wool.—Dye for fifteen minutes at 80° C. in a solution of indophenol-white, rendered either alkaline by the addition of sodium carbonate, or acid by means of acetic acid. Wring out, wash, and develop the colour by exposure to air, or by working the material for a few minutes in cold dilute solution of bichromate of potash, or an ammoniacal solution of sulphate of copper. For dark shades the solution of indophenol-white should be concentrated; the dye-bath is not exhausted, and should always be preserved.

366. Gallocyanin (Durand and Huguenin).—This colouring matter, also called New Fast Violet, is obtained by the action of nitroso-dimethyl-aniline on tannic acid. In dyeing, it yields a bluish-violet colour possessing only moderate brilliancy, but tolerably fast to the action of acids, alkalis, and light. Applied in conjunction with other colouring matters, it is useful for obtaining compound shades.

Application to Cotton.—Mordant the cotton by means of an alkaline solution of chromium oxide, and wash well. Dye in a separate bath with Gallocyanin, at a temperature of 80° C. for 1—1½ hour. If, after dyeing, the cotton is washed, dried, and steamed, the colour becomes somewhat darker and faster.

Application to Wool.—The wool may be dyed without any previous preparation, or it may be first mordanted in the usual manner with bichromate of potash. Dye in a neutral bath. Introduce the wool into a cold solution, raise the temperature gradually to 70° C. in the course of one hour, and continue dyeing for ½—1 hour longer.

Application to Silk.—Dye at 70°—80° C. in a bath containing colour solution and "boiled-off" liquor. The silk may be previously mordanted with chrome alum, though this is not absolutely necessary.

CHAPTER XIX.

AZO COLOURING MATTERS.

(*a*) *Amido-azo-colours.*

367. Aniline Yellow [$C_6H_5{\cdot}N=N{\cdot}C_6H_4{\cdot}NH_2{\cdot}HCl$]. Diamido-azo-benzene-hydrochloride. —This colouring matter is no longer used in dyeing, because the colour which it yields is volatile and not fast. Cotton has no attraction for it. Wool and silk may be dyed in a bath slightly acidified with acetic acid.

368. Chrysoïdine [$C_6H_5{\cdot}N=N{\cdot}C_6H_3(NH_2)_2{\cdot}HCl$].— Diamido-azo-benzene-hydrochloride. This colouring matter, much used in cotton-dyeing for producing various shades of orange, is prepared by the action of diazo-benzene-chloride on *m*-phenylene-diamine. It is well adapted for shading, and may be used as the yellow part in a number of compound shades, *e.g.*, olive, brown, scarlet, &c. Chrysoïdine FF (L. Cassella & Co.) is the corresponding toluene compound.

Application to Cotton.—Mordant the cotton with tannic acid and tartar emetic, and wash; dye at 60° C. in a solution of the colouring matter, without any further addition. Avoid high temperatures, since the colour is thereby rendered duller.

Sometimes the fixing of the tannic acid with tartar emetic may be omitted, and for very light shades it is not even necessary to prepare the cotton with tannic acid, since this fibre seems to possess naturally a certain attraction for Chrysoïdine. Good shades are obtained by applying Chrysoïdine to cotton previously dyed with Catechu, Sumach, &c.

Application to Wool.—Dye at 60°—70° C. in a neutral bath, or with the addition of 2—4 per cent. of soap, or one acidified with alum. These additions tend to brighten the colour. The addition of sulphuric acid to the dye-bath impoverishes the colour, but if, after dyeing according to the above method, the wool be worked for 10—15 minutes in cold water slightly acidified with sulphuric acid, the colour acquires a deeper and redder hue. Dyeing at 100° C. dulls the colour considerably.

Application to Silk.—Dye at a temperature of 60° C., with or without the addition of a little soap to the dye-bath. Brighten in a bath very slightly acidified with sulphuric acid.

369. Phenylene Brown.—

$$[C_6H_4{\cdot}(NH_2){\cdot}N{=}N{\cdot}C_6H_3(NH_2)_2{\cdot}2HCl]$$

Triamido-azo-benzene-hydrochloride.

This colouring matter is prepared by the action of nitrous acid on *m*-phenylene-diamine, and dissolving the base thus produced in hydrochloric acid. It also bears the commercial names: Bismarck Brown, Vesuvine, Canelle, Manchester Brown, Cinnamon Brown, &c. Bismarck Brown G G and E E (L. Cassella & Co.) are the pure products of toluylene-diamine and phenylene-diamine respectively.

Application to Cotton.—Prepare the cotton with tannic acid and tartar emetic; wash and dye in a neutral bath at 50°—60° C. Add the colour solution gradually. A slight addition of alum to the dye-bath may sometimes be made to modify the shade. The shades given by Bismarck Brown are similar to those obtained from Catechu, but, as a rule, brighter. Light shades can be dyed without previous preparation of the cotton. Catechu browns are frequently dyed with it in order to brighten or modify the colour.

A great variety of compound colours are obtainable by using it along with other basic colouring matters, *e.g.*, Magenta, Malachite Green, Methyl Violet, Methylene Blue, &c.

Application to Wool.—Dye in a neutral bath. For a full shade, use 5—8 per cent. of colouring matter. The addition of 8—10 per cent. of alum to the bath makes the shade redder. Enter the wool at 45° C., and heat gradually to 100° C.

Application to Silk.—Dye in a weak soap bath at 60° C., and brighten in a fresh bath slightly acidified with acetic or tartaric acid.

(*b*) *Amido-azo-sulphonic Acids.*

370. Fast Yellow.—

$$[(SO_3Na)C_6H_4{\cdot}N=N{\cdot}C_6H_4(NH_2)]$$
Amido-azo-benzene-sodium-*p*-sulphonate.

This colouring matter is also called Acid Yellow; it cannot be used for dyeing cotton. It is well adapted for using along with other acid colouring matters to obtain compound shades on wool or silk. Employed alone it cannot compete with some other yellows in brilliancy. The above compound is sometimes distinguished as Fast Yellow G, while Fast Yellow R is given to the corresponding toluene compound.

Application to Wool.—Dye in an acid bath. For 0·5—3 per cent. of colouring matter add 2—6 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). Enter the wool at 40° C., and heat gradually to 100° C. in the course of $\frac{3}{4}$—1 hour, and boil for $\frac{1}{4}$ hour. If 5—10 per cent. of alum be used instead of sulphuric acid, the shade given is weaker and less orange.

Application to Silk. — Dye at a temperature of 60°—80° C., in a bath containing "boiled-off" liquor and acidified with sulphuric acid.

371. Dimethylaniline Orange.—

$$[(SO_3{\cdot}NH_4)C_6H_4{\cdot}N=N{\cdot}C_6H_4(N(CH_3)_2)]$$
p-Dimethyl-amido-azo-benzene-ammonium-*p*-sulphonate.

Other commercial names of this colouring matter are: Helianthin, Gold Orange, Orange III., and Tropæolin D, &c.

Application to Cotton.—Work the cotton in cold stannate of soda solution, 5° Tw. (Sp. Gr. 1·025), till thoroughly saturated, and wring out; work for $\frac{1}{4}$—$\frac{1}{2}$ hour in a cold solution of alum (15—20 per cent.) and wring out; dye in a concentrated solution of the colouring matter, with the addition of an equal percentage of alum. Enter cold, and heat gradually to 45° C., but not higher. Dry without previous washing. The colour is not fast to washing.

Application to Wool.—Dye exactly as with Fast Yellow. Somewhat brighter shades are obtained by using stannic chloride instead of sulphuric acid. With 2 per cent. of colouring matter a full reddish-orange is obtained.

Application to Silk.—Dye exactly as with Fast Yellow.

372. Diphenylamine Orange—

$$[(\overset{4}{\overline{SO_3}}K)C_6H_4{\cdot}N=N{\cdot}C_6H_4(N{\cdot}H{\cdot}C_6H_5)]$$

p-Phenyl-amido-azo-benzene-potassium-*p*-sulphonate.

This colouring matter is also called Tropæolin OO, Orange IV., Orange N, Yellow N, &c. It is very sensitive to the action of an excess of *free* acid, which causes it to dye a more orange colour. Large excess of mineral acid causes its solution to become violet through liberation of the free colour acid. Closely allied to this colouring matter are the three following:—

373. Metanil Yellow (BASF).—

$$[(\overset{3}{\overline{SO_3}}Na)C_6H_4{\cdot}N=N{\cdot}C_6H_4(N{\cdot}H{\cdot}C_6H_5)]$$

p-Phenyl-amido-azo-benzene-sodium-*m*-sulphonate.

This colouring matter is also called Tropæolin G (L. Cassella & Co.).

374. Brilliant Yellow (BASF).—

$$[(SO_3Na)C_6H_3(CH_3){\cdot}N=N{\cdot}C_6H_4(N{\cdot}H{\cdot}C_6H_5)]$$

p-Phenyl-amido-azo-toluene-sodium-*p*-sulphonate.

375. Azoflavin 2 (BASF).—

$$[(SO_3Na)C_6H_4{\cdot}N=N{\cdot}C_6H_4(N{\cdot}H{\cdot}C_6H_4(NO_2))].$$

p-Nitro-phenyl-amido-azo-benzene-sodium-*p*-sulphonate.

All these colouring matters are specially suitable for wool- and silk-dyeing, and give fine yellow or orange shades. They are applied in the same way as Fast Yellow and Dimethylaniline Orange. The colours on cotton are not fast to washing. If 10 per cent. of alum is added to the dye-bath instead of sulphuric acid, the colours on wool are rendered brighter.

Indian Yellow (L. Cassella & Co.) is isomeric with Azoflavin.

376. Congo Red (Act. Gesell. Anilin. Fabrik, Berlin).—

$$\left\{\begin{array}{l} C_6H_4{\cdot}N=N{\cdot}C_{10}H_5(NH_2)(SO_3Na) \\ | \\ C_6H_4{\cdot}N=N{\cdot}C_{10}H_5(NH_2)(SO_3Na) \end{array}\right.$$

Tetrazo-diphenyl-dinaphthylamine-sodium-disulphonate.

This colouring matter possesses the very interesting property of being readily applied to the vegetable fibres without the aid of a mordant. It may be used for dyeing mixed goods consisting of cotton and wool, and yields a bright scarlet colour, fairly fast to boiling soap solutions, but not to light. It is also extremely sensitive to the action of acids; these change the colour to blue.

Application to Cotton.—Dye at 100° C. in a neutral bath, or one rendered slightly alkaline by the addition of soap; wash and dry. A much richer colour is got if the cotton is previously mordanted with stannic oxide, or, better still, with sulphated oil and aluminium sulphate.

Application to Wool and Silk.—Dye in a neutral bath or with the addition of a little soap.

377. Benzopurpurin (F. Baeyer & Co.).—

$$\left\{\begin{array}{l} C_7H_6{\cdot}N=N{\cdot}C_{10}H_5(NH_2)(SO_3Na) \\ | \\ C_7H_6{\cdot}N=N{\cdot}C_{10}H_5(NH_2)(SO_3Na) \end{array}\right.$$

Tetrazo-ditolyl-diphenylamine-sodium-disulphonate.

This colouring matter is applied to the various fibres in the same manner as Congo Red, being closely allied to it in chemical constitution. It yields a bright scarlet colour, fairly fast to soap, and less sensitive to light and particularly to acids, than Congo Red. It is not affected by dilute acetic acid, or even by dilute mineral acids. The best addition to make to the dye-bath is phosphate of soda, though one may, if desirable, use soap or silicate of soda instead.

(c) *Oxy-azo Colouring Matters.*

378. These include yellow, orange, red, crimson, and brown colours. Nearly all belong to the class of so-called acid-colours, and are specially suitable for wool- and silk-dyeing. When applied to cotton, most of the colours are not fast to washing with water.

Many of the scarlets have largely displaced Cochineal in wool-dyeing. For plain scarlet dyes (*e.g.* on flannels, &c.) they are even preferable to Cochineal, since the colour does not become dull and bluish on washing with soap. They are, however, not suitable for yarn which has to be woven with other light-coloured yarns, if the material so produced must afterwards be washed with soap, scoured, or milled. During these processes the colour "bleeds," or comes off slightly and dyes very permanently the contiguous light-coloured fibres, thus spoiling the general appearance of the fabric. This defect is common, indeed, to all those coal-tar colouring matters which dye without mordant. For dark-coloured fabrics the defect is not noticeable.

The dyeing properties of many of these colouring matters are very similar.

The dyes they yield are very fairly fast to light, though they differ considerably in this respect. As a rule, the tetrazo compounds are faster to light than the diazo compounds.

It is difficult to identify all the colouring matters of this class met with in commerce, since each manufacturer gives a special name and mark to his own products.

The following list, however, comprises the most important :—

379. Tropæolin Y.—

$$[(SO_3Na)C_6H_4{\cdot}N=N{\cdot}C_6H_4{\cdot}(OH)]$$

p-Phenol-azo-benzene-sodium-*p*-sulphonate.

This colouring matter has now little importance, having been replaced by other similar but superior colouring matters.

380. Resorcinol Yellow.—

$$[(SO_3Na)C_6H_4{\cdot}N=N{\cdot}C_6H_3(OH_2)]$$

Resorcinol-azo-benzene-sodium-*p*-sulphonate.

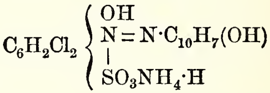
This colouring matter is also called Tropæolin O, Tropæolin R, Chryseolin, Chrysoïn (Poirrier). It gives an orange dye of only moderate brilliancy, and is chiefly used along with other acid-colours to produce olives, maroons, &c.

381. Orchil Brown (F. Baeyer & Co.).—

$$[(NH_2)C_{10}H_6{\cdot}N=N{\cdot}C_6H_4(SO_3Na)]$$

This colouring matter is *a*-naphthylamine-azo-benzene-sodium-sulphonate.

382. Azarin S (M. L. & B.).—



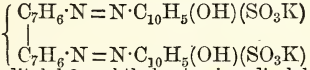
$$C_6H_2Cl_2\left\{\begin{array}{l}OH\\ N=N{\cdot}C_{10}H_7(OH)\\ |\\ SO_3NH_4{\cdot}H\end{array}\right.$$

This colouring matter is suitable only for cotton. It yields a brilliant red said to be fairly fast to light.

The following method of applying it to calico is proposed by the manufacturers :—

Pad the cloth with a solution of aluminium acetate to which a small proportion of stannous oxide has been added. After drying and ageing for 12 hours, work the cloth for half an hour in a cold solution containing a very small proportion of acetate of lime and sodium carbonate; then wash well and dye in a solution of the colouring matter with the addition of a little sulphated oil. After dyeing, wash, dry, pad with a dilute solution of sulphated oil, dry and steam; then wash in a cold weak soap solution and dry. The alkalinity of the soap gives the red a bluish tone, which may be removed by a final passage in very dilute acid.

383. Azo Blue (F. Baeyer & Co.).—



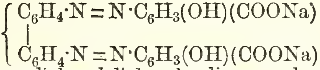
$$\left\{\begin{array}{l} C_7H_6\cdot N=N\cdot C_{10}H_5(OH)(SO_3K) \\ | \\ C_7H_6\cdot N=N\cdot C_{10}H_5(OH)(SO_3K) \end{array}\right.$$

Tetrazo-ditolyl-β-naphthol-potassium-disulphonate.

This is the first *blue* colouring matter of the azo series, which has appeared, possessing the property of dyeing vegetable fibres without the aid of a mordant. It yields a reddish-blue colour, fast to soap and concentrated mineral acids, and moderately fast to light.

It is applied in dyeing in the same manner as Benzopurpurin and Chrysamin, with which it may therefore be used in the same bath for the purpose of obtaining compound shades on cotton, mixed goods, &c.

384. Chrysamin.—(F. Baeyer & Co.).



$$\left\{\begin{array}{l} C_6H_4\cdot N=N\cdot C_6H_3(OH)(COONa) \\ | \\ C_6H_4\cdot N=N\cdot C_6H_3(OH)(COONa) \end{array}\right.$$

Tetrazo-diphenyl-diphenol-sodium-α-carbonate.

This colouring matter dyes the vegetable fibres without the aid of a mordant in the same manner as Congo Red, Benzopurpurin, and Azo Blue.

The colour obtained on cotton by the aid of a boiling soap-bath is a sulphur-yellow remarkably fast to light; also fast to acetic acid, but not to mineral acids.

385. α-Naphthol Orange.—

$$[(SO_3Na)C_6H_4\cdot N=N\cdot \alpha C_{10}H_6\cdot OH)]$$

α-Naphthol-azo-benzene-sodium-p-sulphonate.

This colouring matter is also called Tropæolin OOO *No.* 1, Orange *No.* 1 (Poirrier). It dyes a very reddish-orange shade.

386. β-Naphthol Orange.—

$[(SO_3Na)C_6H_4{\cdot}N{=}N{\cdot}\beta C_{10}H_6{\cdot}OH]$
β-Naphthol-azo-benzene-sodium-*p*-sulphonate.

This colouring matter also bears the names: Tropæolin OOO *No.* 2, Orange *No.* 2 (BASF) (Poirrier), Orange extra (L. Cassella & Co.), Mandarin S (Act. Gesell, Berlin), Chrysaureïn. It dyes a bright reddish-orange shade, similar to that yielded by Tropæolin OOO No. 1. A mixture of Tropæolin OOO No. 2 and Fast Red is sometimes sold under the name of French Red (*rouge Français*). Tropæolin OOO No. 2 is largely used, both alone and along with Indigo Carmine and other acid-colours, for producing browns, olives, &c.

387. Tropæolin 0000.—

$[C_6H_5{\cdot}N{=}N{\cdot}\beta C_{10}H_5(OH)(SO_3Na)]$
Benzene-azo-β-naphthol-sodium-α-sulphonate.

Orange G (M. L. & B.).—

$[C_6H_5{\cdot}N{=}N{\cdot}\beta C_{10}H_4(OH)(SO_3Na)_2]$
Benzene-azo-β-naphthol-sodium-β-disulphonate.

This colouring matter dyes a bright orange, somewhat less red than Tropæolin OOO No. 2, which is extremely fast to light.

388. Scarlet G T (F. Baeyer & Co.).—

$[C_6H_4(CH_3){\cdot}N{=}N{\cdot}\beta C_{10}H_5(OH)(SO_3Na)]$
Toluene-azo-β-naphthol-sodium-β-sulphonate.

389. Xylidine Scarlet G (M. L. & B.).—

$[C_6H_3(CH_3)_2{\cdot}N{=}N{\cdot}C_{10}H_5(OH)(SO_3Na)]$
o-Xylene-azo-β-naphthol-sodium-β-sulphonate.

Scarlet R (F. Baeyer & Co.) is the isomeric *m*-xylene compound.

This colouring matter seems to be identical with Scarlet 2 R (Act. Gesell. Farben Fabrik, Berlin). Scarlet G (BASF) is the closely-allied *p*-xylene-azo-β-naphthol-sodium-α-disulphonate.

Xylidine Scarlet R (M. L. & B.).—This colouring matter is isomeric with the last, and is the sodium salt of the corresponding β-disulphonic acid compound. It is sometimes simply called Scarlet R. As the mark (R) implies, it dyes a redder shade than Scarlet G. Scarlet R (BASF) is the isomeric *p*-*m*-xylene-azo-β-naphthol-sodium-disulphonate.

390. Scarlet G G (M. L. & B.).—

$$[C_6H_2(CH_3)_3{\cdot}N{=}N{\cdot}C_{10}H_4(OH)(SO_3Na)_2]$$

Cumene-azo-β-naphthol-sodium-β-disulphonate.

This colouring matter seems to be identical or isomeric with Scarlet 4 R (Act. Gesell. Farben Fabrik, Berlin).

Scarlet R R.—This colouring matter is isomeric with the last, and is the sodium salt of the corresponding α-disulphonic acid.

Another very closely allied colouring matter, also called Scarlet R R, is the following:

$$[C_6H_2{\cdot}(CH_3)_2(C_2H_5){\cdot}N{=}N{\cdot}C_{10}H_4(OH)(SO_3Na)_2]$$

Ethyl-xylene-azo-β-naphthol-sodium-α-disulphonate.

Scarlet 3 R (M. L. & B.).—

$$[C_6H_2(C_2H_5)(CH_3)_2{\cdot}N{=}N{\cdot}C_{10}H_4(OH)(SO_3Na)_2]$$

Ethyl-dimethyl-azo-β-naphthol-sodium-disulphonate.

Scarlet 3 R (BASF).—

$$[C_6H_2(CH_3)_3{\cdot}N{=}N{\cdot}C_{10}H_4(OH)(SO_3Na)_2]$$

Pseudo-cumene-azo-β-naphthol-sodium-disulphonate.

Scarlet 4 R (M. L. & B.).—

$$[C_6H_2(CH_3)_3{\cdot}N{=}N{\cdot}C_{10}H_4(OH)(SO_3Na)_2]$$

Cumene-azo-β-naphthol-sodium-disulphonate.

391. Fast Brown (M. L. & B.).—

$$[(SO_3Na)C_6H_2(CH_3)_2{\cdot}N{=}N{\cdot}\alpha C_{10}H_6(OH)]$$

α-Naphthol-azo-xylene-sodium-sulphonate.

Fast Red (BASF).—

$$[(SO_3Na)C_{10}H_6{\cdot}N{=}N{\cdot}\beta C_{10}H_6(OH)]$$

β-Naphthol-azo-naphthalene-sodium-sulphonate.

This colouring matter is also called Roccellin (Poirrier), Orseillin No. 3, Rubidin, Rauracienne, &c. It does not yield a brilliant red, but one which is remarkable for its fullness or body. It is very useful in conjunction with other acid-colours for producing compound shades.

Fast Brown (BASF).—This colouring matter is the corresponding *a*-naphthol compound.

392. **Fast Red C** (BASF).—

$$[(NH_2)C_{10}H_6\cdot N{=}N\cdot \alpha C_{10}H_5(OH)(SO_3Na)]$$

α-Naphthylamine-azo-α-naphthol-sodium-sulphonate.

Croceïn 3 BX (F. Baeyer & Co.).—

$$[(SO_3Na)C_{10}H_6\cdot N{=}NC_{10}H_5(OH)(\overset{a}{SO_3}Na)]$$

Naphthalene-sodium-sulphonate-azo-β-naphthol-sodium-α-sulphonate.

393. **Claret Red B** (M. L. & B.).—

$$[C_{10}H_7\cdot N{=}N\cdot C_{10}H_4(OH)(\overset{a}{SO_3}Na)]$$

α-Naphthalene-azo-β-naphthol-sodium-α-disulphonate.

This colouring matter is also called Bordeaux R. If alum is used in the dye-bath for wool, the colour is apt to be very uneven.

Fast Red B (BASF).—This colouring matter is isomeric with the last, being the sodium salt of the corresponding β-sulphonic acid. Other names which seem to be given to it are Claret Red R (M. L. & B.) and Bordeaux G.

Crystal Scarlet 6 R (L. Cassella & Co.).—This colouring matter is also isomeric with Claret Red B, being the sodium salt of the corresponding γ-disulphonic acid.

Amaranth (M. L. & B.) also (L. Cassella & Co.).—

$$[(SO_3Na)C_{10}H_6\cdot N = N\cdot C_{10}H_4(OH)(SO_3Na)_2]$$

Naphthalene-azo-β-naphthol-sodium-trisulphonate.

New Coccin (M. L. & B.); **Fast Red D** (BASF).—These colouring matters are isomeric with the last.

Brilliant Scarlet 4 R (L. Cassella & Co.).—This colouring matter is also isomeric with Amaranth, being the sodium salt of the corresponding γ-disulphonic acid.

Scarlet 6 R (M. L. & B.).—

$$[(SO_3Na)C_{10}H_6\cdot N = N\cdot C_{10}H_3(OH)(SO_3Na)_3]$$

Naphthalene-azo-β-naphthol-sodium-tetrasulphonate.

394. Anisol Red (BASF).—

$$[C_6H_4(OCH_3)\cdot N{=}N\cdot C_{10}H_5(OH)(SO_3Na)]$$

Anisol-azo-β-naphthol-sodium-sulphonate

Phenetol Red (BASF).—

$$[C_6H_4(OC_2H_5)\cdot N{=}N\cdot C_{10}H_4(OH)(\overset{\alpha}{\overline{SO_3Na}})_2]$$

Phenetol-azo-β-naphthol-sodium-α-disulphonate.

This colouring matter is also called Coccinin (M. L. & B.).

Coccinin B (M. L. & B.).—This colouring matter is closely allied to the last, being the corresponding methyl-*p*-cresyl $C_6H_3(OCH_3)(CH_3)$ compound.

395. Brilliant Croceïn M (L. Cassella & Co.).—

$$[C_6H_5\cdot N{=}N\cdot C_6H_4\cdot N{=}N\cdot C_{10}H_4(OH)(SO_3Na)_2]$$

Benzene-azo-benzene-azo-β-naphthol-sodium-γ-disulphonate.

Scarlet S (Act. Gesell. Farben Fabrik, Berlin).—This colouring matter is isomeric with the last.

Scarlet 5 R (M. L. & B).—

$$[C_6H_5\cdot N{=}N\cdot C_6H_4\cdot N{=}N\cdot C_{10}H_3(OH)(SO_3Na_3)]$$

Benzene-azo-benzene-azo-β-naphthol-sodium-trisulphonate.

396. Biebrich Scarlet (Kalle & Co.).—

$$[(SO_3Na)C_6H_4\cdot N{=}N\cdot C_6H_3(SO_3Na)\cdot N{=}N\cdot C_{10}H_5(OH)]$$

β-Naphthol-azo-benzene-azo-benzene-sodium-disulphonate.

This colouring matter is identical with Imperial Scarlet (F. Baeyer & Co.).

Fast Scarlet (BASF).—

$$[(SO_3Na)C_6H_4\cdot N{=}N\cdot C_6H_4\cdot N{=}N\cdot C_{10}H_5(OH)]$$

β-Naphthol-azo-benzene-azo-benzene-sodium-sulphonate.

397. Croceïn Scarlet 3 B (F. Baeyer & Co.).—

$$[(\overset{4}{\overline{SO}}_3Na)C_6H_4\cdot N{=}N\cdot C_6H_4\cdot N{=}N\cdot C_{10}H_5(OH)(\overset{\alpha}{SO_3\overline{Na}})]$$

Benzene-sodium-*p*-sulphonate-azo-benzene-azo-β-naphthol-sodium-α-sulphonate.

Croceïn Scarlet 7 B (F. Baeyer & Co.).

$$[(SO_3Na)C_6H_3(CH_3)N{=}N\cdot C_6H_3(CH_3)\cdot N{=}N\cdot C_{10}H_5(OH)(SO_3Na)]$$

Toluene-sodium-*p*-sulphonate-azo-toluene-azo-β-naphthol-sodium-α-sulphonate.

Scarlet SS (Act. Gesell. Farben Fabrik, Berlin).—This colouring matter is isomeric with the last. A mixture of Xylidine Scarlet and Acid Magenta is said to have been sold under the same name.

398. *Application of the Oxy-azo Colours to Cotton.*—Work the cotton $\frac{1}{4}$—$\frac{1}{2}$ hour in a cold solution of stannate of soda, 6°—8° Tw. (Sp. Gr. 1·03—1·04), wring out and pass into a cold solution of alum, 4°—6° Tw. (Sp. Gr. 1·02—1·03) for a quarter of an hour. Wring out, and, without washing, dye at 45°—50° C., in a concentrated solution of the colouring matter, with the addition of 5—10 per cent. of alum. Wring out, and *dry without washing.* The colour does not withstand even washing with water. The cotton may also be previously prepared with sulphated oil, instead of with stannic oxide, and then dyed in the manner described.

An interesting method of obtaining faster colours on cotton with these colouring matters is that included in the patents of Grässler and others.

The colouring matters used for wool and silk are the alkali salts of complex sulphonic acids, and are produced in a cold alkaline solution by the mutual reaction of azo compounds upon phenols.

The colouring matter obtained is soluble if either the azo compound or the phenol, or both, are in the form of sulphonates, but if otherwise, it is insoluble.

The insoluble non-sulphonated colour can be precipitated at once upon the cotton fibre, by first impregnating the latter with a cold alkaline solution of the phenol, wringing out, and then passing it into a solution of the azo compound. In practice, it is desirable to pass again into the phenol solution, wring out, wash and soap slightly, in order to remove loosely adhering colour.

Somewhat brighter and fuller colours are also obtained by preparing the cotton previously with sulphated oil. Owing to its instability, the solution of the azo compound should be prepared only a short time before use.

The dye produced on the cotton in this way bears washing with water, and even with soap solutions, but it is liable to rub off; it also withstands the action of light fairly well.

The following equation represents the formation of Xylidine Red in this way :—

$$\underset{\text{Diazo-xylene-chloride.}}{C_6H_3(CH_3)_2{\cdot}N = N{\cdot}Cl} + \underset{\text{Sodium-}\alpha\text{-naphthol.}}{C_{10}H_7{\cdot}ONa} =$$

$$= \underset{\text{Xylidine red.}}{C_6H_3(CH_3)_2{\cdot}N = N{\cdot}C_{10}H_6{\cdot}OH} + NaCl.$$

Application to Wool.—Dye with 1—2 per cent. of colouring matter, with the addition of 2—4 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), and 15—30 per cent. of sodium sulphate. Enter the wool at 40°—50° C., raise the temperature gradually, in the course of an hour, to 100° C., and boil a quarter of an hour.

Several of the colouring matters give brighter colours if the sulphuric acid is replaced by 5—10 per cent. of alum, or 5—10 per cent. of stannic chloride, 120° Tw. (Sp. Gr. 1·6). Care must always be taken to have the bath sufficiently acid to develop the full colouring power; and if there is any tendency to uneven dyeing, the temperature should be raised very gradually.

Application to Silk.—Dye in a bath containing "boiled-off" liquor, slightly acidified with sulphuric acid.

The above modes of application do not, of course, apply to Azarin S, Azo Blue, and Chrysamin.

CHAPTER XX.

ANTHRACENE COLOURING MATTERS.

399. Alizarin [$C_{14}H_6O_2(OH)_2$].—This valuable colouring matter, formerly only known as a substance obtainable from madder root, is now made in large quantities from the coal-tar product, anthracene.

Alizarin is the best type of those colouring matters which dye only with the aid of a mordant, and which yield various colours according to the mordant employed (polygenetic colouring matters). In itself it has little or no colouring power, having no affinity for the vegetable fibres, and merely imparting a comparatively fugitive orange-brown colour to the animal fibres. It possesses, however, the valuable property of forming variously-coloured insoluble precipitates or lakes when combined with many of the metallic oxides, and it is on this property that its use in dyeing depends. Its compound with alumina is red, with stannous oxide orange, with chromic oxide claret-brown, and with ferric oxide violet. All the colours produced on the textile fibres by means of these mordants are extremely fast to light, boiling with soap solutions, milling, &c.

Very closely allied to Alizarin are the colouring matters: *Isopurpurin* or *Anthrapurpurin*, *Flavopurpurin*, and *Purpurin* $C_{14}H_5O_2\cdot(OH)_3$. Their method of application is so similar to that employed for Alizarin, that only special reference will be made to each, where points of difference arise. They are sold separately or mixed together in various proportions, each manufacturer giving his own brand to the different qualities and mixtures. It is customary, for the sake of simplicity, to sell them, whether separate or mixed, under the common name, "Alizarin."

Those which consist entirely, or most largely, of alizarin are called the *blue shades of alizarin*, while those in which Flavo-purpurin, or Isopurpurin predominate, constitute the *yellow shades of alizarin.* These designations have arisen because the former dye alumina mordanted cotton, a crimson or *bluish* shade of red, while the latter give a scarlet or *yellow* shade of red.

Application to Cotton.—Alizarin serves principally for the production of the brilliant Turkey-red dye, already referred to under the head of Madder. For this purpose it has entirely supplanted Madder and its commercial preparation Garancin, because the colours it yields are far more brilliant, quite as fast, and less expensive.

Turkey-red dyeing probably had its origin in India. At an early date it was introduced into Turkey (hence its name), and about the middle of the eighteenth century it began to be practised in France.

Since the publication of the process in the year 1765 by the French Government, it has been carried on largely in Switzerland, Germany, and Britain. At the present time, the chief seats of this important industry are the Vale of Leven, near Glasgow, and Elberfeld in Germany.

Numerous alterations and improvements have been gradually introduced, until it has now reached a very high state of perfection indeed. All the details of the process now employed have been empirically determined throughout a long period, and the successful production of the best Turkey-red depends upon their careful execution.

Cotton is dyed Turkey-red in the form of yarn and cloth. The process for *yarn*-dyeing seems to have experienced little change since the time when Madder was the dyestuff employed, and may serve as a type of the older methods of Turkey-red dyeing. It may be distinguished as the *Emulsion process.*

The present method of Turkey-red *cloth*-dyeing differs considerably in the earlier stages from that in vogue for yarn, and is known as *Steiner's process* (from the name of its inventor). Practical difficulties have prevented the adoption of this improved process for yarn-dyeing.

There is, however, a third process of Turkey-red dyeing applicable to both cloth and yarn, which represents the method most recently introduced. This may be termed the *Sulphated-oil process.* It is not impossible that this last process, or some modification of it, may gradually entirely displace the others; one cannot, however, speak with absolute certainty on this point, and at present all three are in use.

400. Emulsion Process for Dyeing 500 kilos. of Turkey-red Yarn.—The grey yarn is first "laced," *i.e.* the skeins constituting each "head" or "hank" are loosely fastened together by the intertwining of a short piece of cotton cord, in order to prevent entanglement during the several operations. The ends of the cord are also knotted, once or several times, for the purpose of subsequently recognising the various lots.

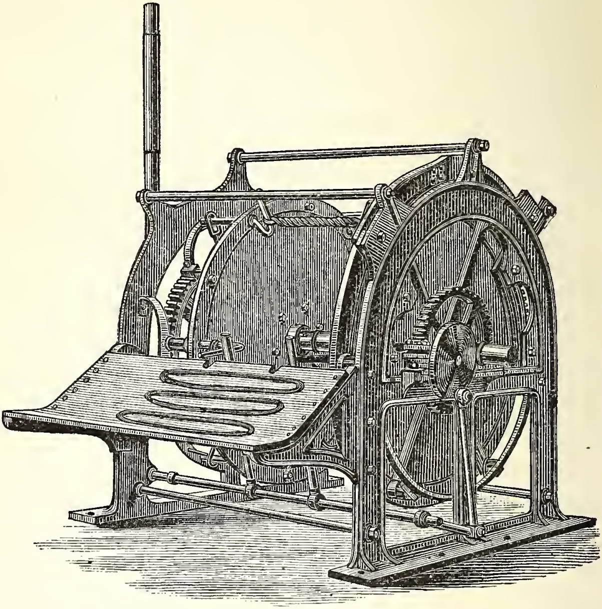


Fig. 86.—Turkey-red Yarn-Wringing Machine.

1*st Operation: Boiling.* — Boil the yarn 6—8 hours with a solution of carbonate of soda, 1° Tw. (Sp. Gr. 1·005), then wash well with water, squeeze and dry in a stove at 55°—60° C.

2*nd Operation: First green liquor.*—This liquor is an emulsion (*see* p. 234) made up with 75 kilos. of olive oil, 8 kilos. of sheep-dung, about 1,000 litres of water, and a sufficiency of a concentrated solution of carbonate of soda to make the whole to 2° Tw. (Sp. Gr. 1·01).

Work the hanks of yarn separately in this emulsion at a temperature of 30°—40° C., till thoroughly saturated (about half a minute), and wring out as evenly as possible. This process is usually called "tramping" (Fr., *tremper*, to steep).

Fig. 86 represents the taking-off end of an excellent wringing machine made by Messrs. Duncan Stewart and Co., Glasgow, and used in some Turkey-red works in this country.

It consists of two large discs revolving on a common shaft. On the periphery of each, and directly opposite each other, are several large iron hooks connected with springs, cog-wheels, and rackwork, in such a manner that those on one of the discs are capable of twisting, while at the same time both sets of hooks yield inwards as the two discs revolve. The hanks of yarn are properly steeped in the emulsion by hand, and at once placed on a pair of the hooks; as the discs make a quarter of a revolution, the hooks twist and squeeze out the excess of liquor; during the next quarter of the revolution the hooks untwist themselves, and at the opposite side of the machine the hanks are thrown or pushed off by a pair of strong upright arms.

Fig. 87 represents a tramping machine of A. Weser, Elberfeld, and used in Germany, which performs the steeping as well as the wringing, hand-labour being required only for putting on and taking off the hanks of yarn. It consists essentially of the liquor trough E, above which are situated the fixed revolving roller B, and loose roller A, on which the hanks are suspended. D is an L-shaped arm, the horizontal portion of which passes within the loop of the hank and depresses it into the liquor. C is an iron cylinder pressing against B, and serves to impregnate the yarn with the solution.

The various movements of the machine are regular and automatic. The hank of yarn is placed on the rollers A

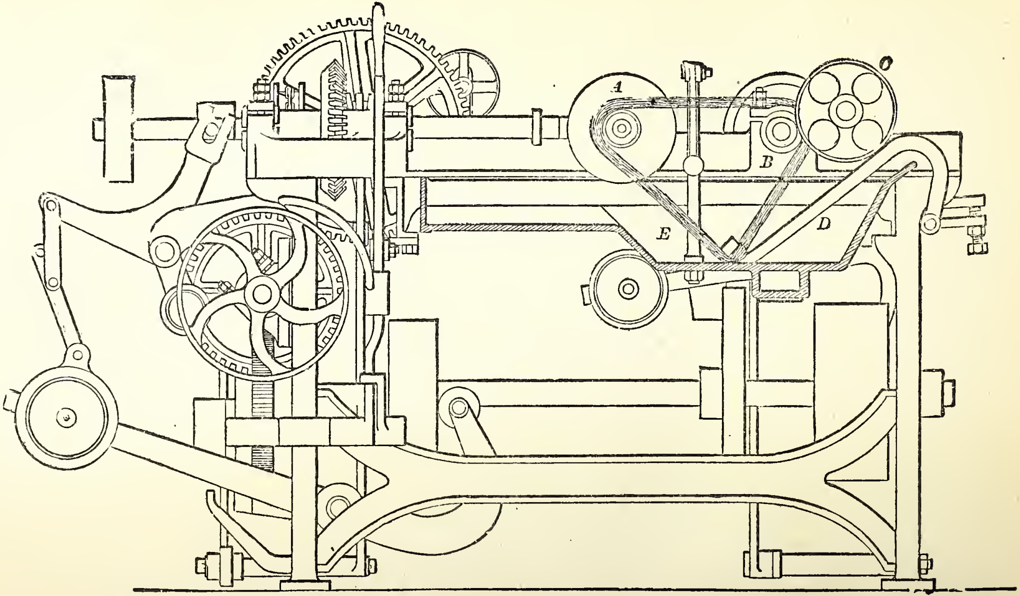


Fig. 87.—Tramping Machine for Turkey-red Yarn.

and B when the arm D is in the horizontal position; the arm D at once falls and steeps the yarn in the liquid, and the rollers revolve for a short period; the arm D now again takes the horizontal position, the roller B ceases to revolve, and the roller A first twists then untwists the hank, and it is ready to be removed by the attendant.

Whichever of the above machines is used, the work of "tramping" the yarn is practically continuous.

The prepared hanks are allowed to remain piled together over-night (12—20 hours), and are then dried in the stove. In this operation (*stoving*) the temperature is raised gradually to 55°—60° C., which is maintained for two hours. Care must be taken to allow the escape of the steam which is given off during the first stages of drying, otherwise the yarn is apt to be tendered.

3rd and 4th Operations: Second and third green liquors.—These are almost exact repetitions of the second operation, the liquor employed being made up separately and with the same proportions of the several ingredients as given above. The sole difference is that it is not necessary to let the prepared yarn lie in pile over-night; instead of this, if it is not raining, it is suspended on tin rods, and exposed to the open air for about 2—4 hours previous to stoving.

It is evident that, after stoving, the dry yarn is charged with sodium carbonate, and since it is very important that all the liquors should be maintained regularly at the same specific gravity, it is customary not to allow the liquor expressed during the wringing of the hanks to flow back into the "tramping" box, except in the case of the "first green liquor," but to collect it separately, and then, if necessary, to dilute it with water before using again.

The total amount of oil used is about thirty per cent. of the weight of yarn, but only a portion of this becomes fixed on the fibre.

5th, 6th, 7th, and 8th Operations: First, second, *third, and fourth white liquors.*—The solution here used is simply carbonate of soda, at 2° Tw. (Sp. Gr. 1·01), but after working the yarn in it a short time, it necessarily becomes an oil emulsion from the oil stripped off the cotton, apart from the fact that it is always mixed with the surplus and expressed liquor from the similar operations with previous lots of yarn.

The yarn is "tramped" in the liquor, wrung out, exposed in the open air, and dried in the stove, as in the previous operations.

9*th Operation: Steeping.*—Steep the yarn during 20—24 hours in water heated to 55° C., wash well, and dry in the stove at about 60° C. If the yarn contains much unmodified oil, a solution of carbonate of soda at $\frac{1}{2}$° Tw. (Sp. Gr. 1·0025) may be used; in this case a second steeping for two hours in tepid water is requisite before washing, &c.

10*th Operation: Sumaching.* — A decoction of Sumach is made by boiling 60 kilos. of best leaf Sumach for about half an hour, with sufficient water to make the cold filtered solution stand at 1$\frac{1}{2}$° Tw. (Sp. Gr. 1·0075). The stoved yarn, while still warm, is steeped in large vats in this decoction as hot (40°—50° C.) as it can be borne by the boys who usually tramp it with bare feet beneath the surface of the solution. After steeping about 4—6 hours, the solution is drained off, and the excess is removed by a hydro-extractor.

11*th Operation: Mordanting* or *Aluming.*—A basic solution of alum is made by dissolving ordinary rock-alum in hot water, and when nearly cold, adding gradually a cold solution of one-fourth its weight of carbonate of soda crystals. The solution is made to stand at 8° Tw. (Sp. Gr. 1·04). Sometimes, though this is not essential, a further addition is made of about 150—200 cubic centimetres of "red liquor," 16° Tw. (Sp. Gr. 1·08), and 5—7 grams of tin-crystals ($SnCl_2$) per kilo. of alum. The sumached yarn while still damp is tramped in the alum solution at a temperature of 40°—50° C., and left to steep for twenty-four hours. It is then thoroughly washed and hydro-extracted.

12*th Operation : Dyeing.*—Dye with 150—180 grams of Alizarin (10 per cent.), 30 grams of ground Sumach,

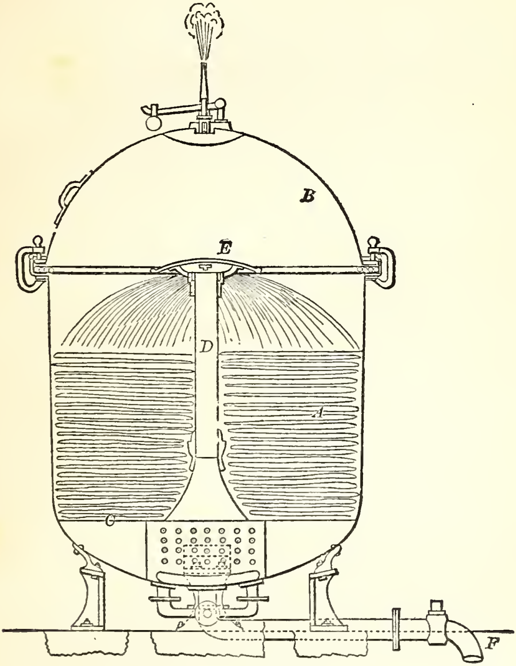


Fig. 88.—Clearing Boiler.

and about 300 grams of bullock's blood, per kilo. of cotton yarn. If the water contains little or no lime, add also ground chalk in the proportion of 1 per cent. of the weight of Alizarin (10 per cent.) employed. The yarn is introduced into the cold solution of the dye-vessel, the temperature is gradually raised to 100° C., in the course of one hour, and the boiling is continued for $\frac{1}{2}$—1 hour. After dyeing, the yarn is washed, although this is not absolutely necessary.

13*th Operation: First Clearing.*—Boil the yarn for four hours at 3—4 pounds' pressure with about 30 grams of carbonate of soda crystals, and 30 grams of palm-oil soap, dissolved in a sufficiency of water, per kilo. of yarn. Wash afterwards. The "clearing boiler" used, and shown in Fig. 88, and in plan in Fig. 89, is similar in construction to an ordinary low-pressure bleaching kier; it is, however, made of copper instead of iron. A represents the yarn; B the lid provided with safety valve and blow-off pipe; C the perforated false bottom; D the puffer-pipe; E the bonnet for distributing the liquor over the yarn; F the draw-off pipe. During the boiling, the liquor which collects below the false bottom is forced by the steam up to the top of the puffer-pipe, there to be ejected and spread over the goods. This action is of an intermittent character, since, after each ejection of the liquor, the pressure of the steam must accumulate below the false bottom until it is again able to overcome the weight of the column of water in the puffer-pipe.

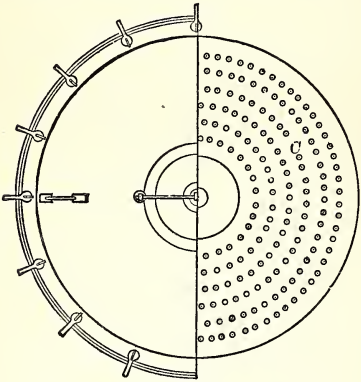


Fig. 89.—Plan of Fig. 88.

14*th Operation: Second Clearing.*—Boil the yarn for 1—2 hours at 3—4 pounds' pressure with a solution containing 25 grams of palm-oil soap and $1\frac{1}{2}$ grams of tin-crystals per kilo. of yarn. Wash well and dry in an open-air shed. Previous to drying, the large excess of water is removed by means of the hydraulic press represented in Fig. 90. It consists of a strong iron framework D D, with a strong, fixed, but adjustable head A above, and a similar one B below, attached to the hydraulic piston C, and thus capable of being moved up or down. By means of this machine a very large quantity of wet yarn may be rapidly and efficiently squeezed.

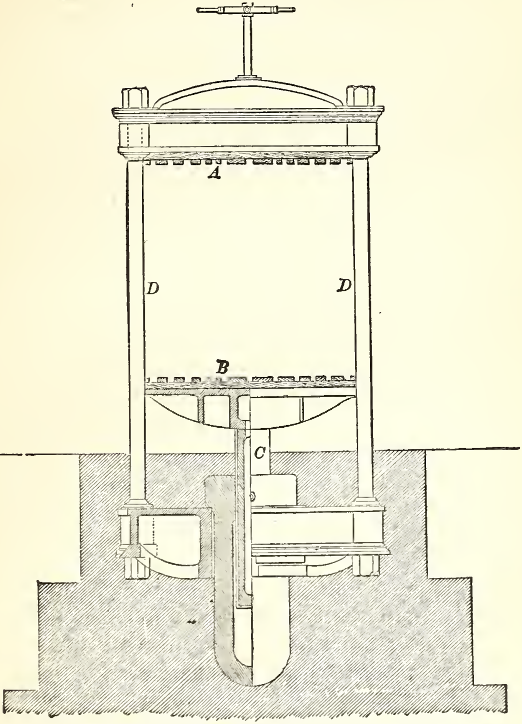


Fig. 90.—Hydraulic Press.

The above fairly represents the "Emulsion process" of Turkey-red yarn-dyeing as practised at the present time. It consists, therefore, of a somewhat numerous series of operations, occupying usually about three weeks' time, and although, hitherto, no absolutely satisfactory scientific explanation has been given of the exact nature of the chemical changes effected by every detail of the whole process, still their general character is tolerably well understood. The object of the frequent steeping in oil-emulsion, drying in the open air, and stoving, is to impregnate the fibre evenly and thoroughly with oil, and to modify it in such a manner that it is not affected or removed by weak alkaline solutions, and that it will attract alumina from its solutions.

Many kinds of oil have been employed, but long experience has proved that olive oil gives the best and most certain results. The particular quality of oil most suitable for the purpose is that obtained by a second pressing of the olives after they have somewhat fermented and been steeped in boiling water. (Fr., *huile tournante*). It contains nitrogenous and extractive matters, which cause it gradually to become rancid, particularly when exposed to the air, *i.e.*, it decomposes, and a portion of the glycerine and fatty acids (margaric and oleïc acids) is liberated. One of the chief characteristics of a good olive oil suitable for Turkey-red, is, that when one measure of it is shaken up with about 16 measures of sodium or potassium carbonate solution at 3° Tw. (Sp. Gr. 1·015), it forms a white milky liquid or emulsion, from which the oil does not readily separate even after standing for 12—18 hours. The oil which forms the most perfect and permanent emulsion with the least quantity of potash or soda is the best. This property of emulsifying, however, can be readily imparted to any oil by mixing it with 5—15 per cent. of oleïc acid.

The exact nature of the chemical changes which the oil undergoes during exposure to the air and stoving is unknown. It is probable, however, that under the influence of the alkaline carbonate and heat, the oil is decomposed and oxidised in such a manner that there remains on the fibre essentially an insoluble oxyoleic acid. Whatever may be the exact chemical composition of the modified oil, it has the property of fixing or combining with alumina, and the compound thus produced can further combine with Alizarin to form a red-lake. The effect which it has of giving brilliancy and fastness to the ultimate colour is probably, in part at least, due to its physical action of enveloping the coloured lake with a transparent oily varnish, which protects it more or less from external influences. All unchanged oil must be removed before mordanting (*see* Operation 9).

The impregnation of the cotton with tannin matter fixes an additional amount of alumina on the fibre, and tends to give deeper and fuller shades. Its use is, however, by no means absolutely essential, as seemed to be the case when Garancin or Madder was used, and by some dyers it is not used.

During the steeping in alum solution an insoluble basic aluminium compound is formed with the modified oil and also with the tannic acid if present. The complex mordant thus fixed on the cloth at this stage combines with Alizarin in the subsequent dye-bath to form the Turkey-red lake. The bullock's blood used is said to prevent, by reason of the coagulation of its albumen, certain impurities accompanying the Alizarin from being fixed on the cotton, but some practical Turkey-red dyers say that blood-albumen, glue, and other substitutes which have been tried, cannot entirely replace it. It certainly adds brilliancy and purity to the colour.

The "First Clearing" operation is for the purpose of removing any remaining impurities which the mordant may have attracted in the dye-bath, but for which its affinity is far less than for Alizarin.

The "Second Clearing" is said by some to introduce into the already extremely complex coloured lake a small portion of stannous oxide. Others allege that there is simply a tin-oleate produced, which is melted and spread over the fibre, as it were, without entering into chemical combination with the red-lake. Liechti has proved analytically that as much as 60 per cent. of the fatty acid of the soap employed, may disappear and become fixed in this manner upon the fibre.

The practical object of this operation is to give the colour the maximum purity and brilliancy of which it is capable.

401. Steiner's Process for Dyeing 500 kilos. of Turkey-red Cloth.—The main difference between this and the "emulsion process" already described, resides in the mode of applying the oil. In the process now to be described the cloth is impregnated with the requisite amount of oil at *one* operation, namely, by padding it in clear hot oil instead of in an oil-emulsion, after which it receives several passages through weak solutions of alkaline carbonate.

This method is capable of yielding a Turkey-red dye of exceptional brilliancy and intensity—better, indeed, than it is possible to obtain by the "emulsion process."

1*st Operation. Bleaching.* — The pieces are well washed and boiled during 2—3 hours, with water only; then boiled for 10—12 hours with 22 litres of caustic soda, 70° Tw. (Sp. Gr. 1·35), and washed: then boiled a second time for 10 hours with 16 litres of caustic soda, 70° Tw., and washed; and finally steeped for two hours in sulphuric acid, 2° Tw. (Sp. Gr. 1·01), well washed and dried.

In order to avoid tendering the fibre in the next operation by reason of traces of acid left in the cloth, it is padded with carbonate of soda solution at 4° Tw. (Sp. Gr. 1·02), and then dried.

2*nd Operation. Oiling.*—The cloth is padded in the open width in olive oil maintained at a constant temperature of 110° C.

Fig. 91 represents a section of the oil-padding machine of Messrs. Duncan Stewart and Co. It consists of a double-jacketed tank B (inside copper, outside iron) for containing the oil. It is heated by means of steam, and is provided with a series of rollers at the top and bottom. Above is a pair of heavy squeezing rollers C. The cloth is passed through as indicated in the figure, being well opened out and made free from creases before entering the oil, by means of the straining bars A A A, and afterwards loosely plaited down by the folder D.

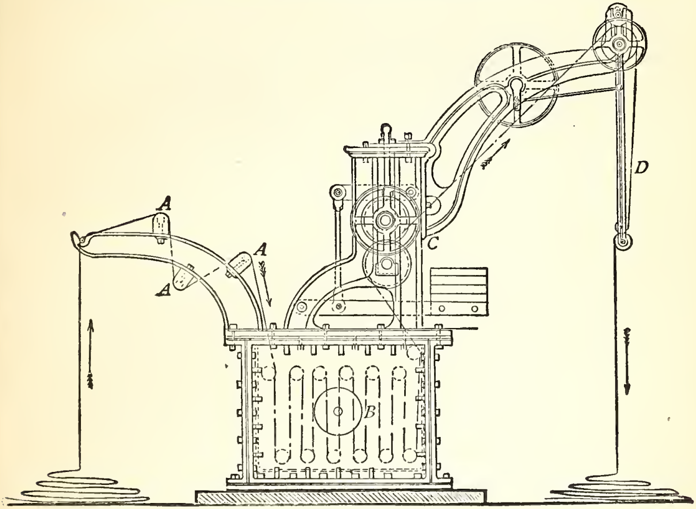


Fig. 91.—Oil-padding Machine.

After padding, the cloth is detached in ten-piece lengths, and hung in the drying stove, the temperature of which is raised as rapidly as possible to 70° C., and this is maintained for two hours.

3rd to 9th Operation. Liquoring.—Pad the cloth seven times in the open width through a solution of carbonate of soda at 4° Tw., and hang in the stove after each padding operation, maintaining the temperature in each case for two hours at 75°—77° C.

In winter the padding liquors are made warm (35°—40° C.), but in summer they are always cold, since if too hot, oil is stripped off the piece to an excessive and injurious degree. In the course of regular working, the liquors soon become veritable oil-emulsions, and constant oversight is necessary in order to maintain their specific gravity as constant as possible, and thus ensure ultimately a regular and satisfactory colour.

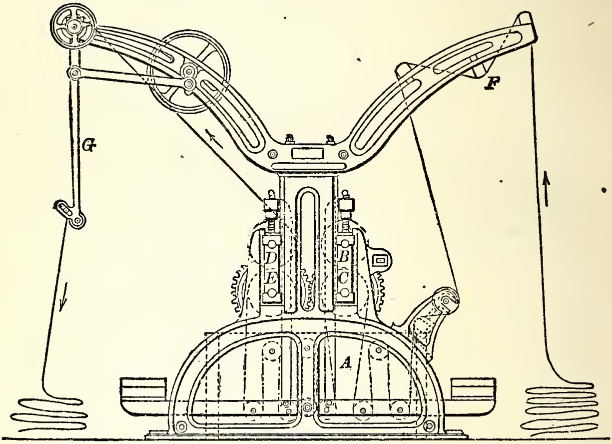


Fig. 92.—Section of Liquor-padding Machine.

A section of the liquor-padding machine of Messrs. Duncan Stewart and Co. is shown in Fig. 92. It consists of a wooden box or tank A to hold the liquor, provided with rollers above and below. Over this are supported two pairs of heavy squeezing rollers B C and D E. At F a few straining bars serve to open out and stretch the cloth; G is the folder. The mode of passing the pieces through the machine is readily understood from the diagram.

With regard to the stoving, it is well to bear in mind that during the first stages of drying much vapour is given off, and special attention must be given to ensure adequate ventilation. Fig. 93 is the ground plan, showing heating flues, and sectional elevation of a modern four-storeyed Turkey-red stove. A A represent ordinary coal fires situated in the basement; the hot flue-gases pass first through channels made of fire-brick, then through iron pipes, and finally make their exit to the chimney at B. The upper part of the stove is divided, by floors of iron-grating, into several storeys C, D, E, F, each of which is furnished with wooden framework, supporting, one above the other, two pairs of horizontal rails provided with short, upright, wooden pegs. Over these pegs one selvedge of the

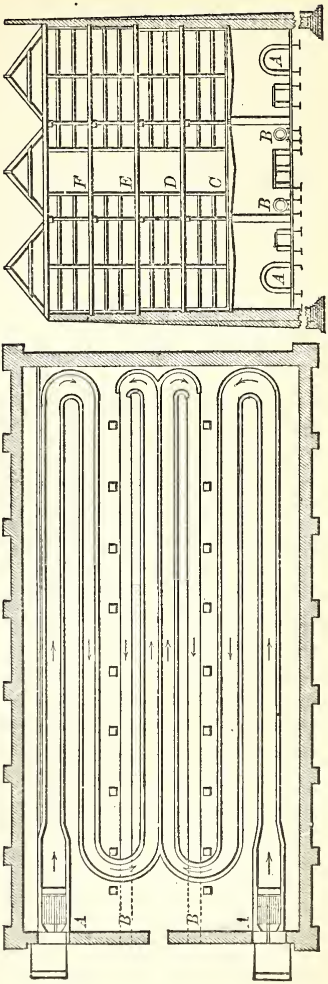


Fig. 93.—Ground Plan and Sectional Elevation of Turkey-red Stove.

cloth is firmly hooked alternately from right to left, while the other is allowed to hang down; thus, when the stove is filled, each storey is closely packed with two tiers of cloth suspended in such a manner that the heated air from below can readily pass between each fold.

A yarn stove is similarly constructed, but in this case the ends of the rods holding the yarn are supported on horizontal rails free from pegs.

Another mode of hanging cloth, but one which is not so economical of space, is to have only one storey in the stove. Above, near the roof, are fixed a number of strong, smooth, wooden rails, on which the cloth is suspended in long folds, reaching down to within one or two feet of the iron-grating immediately above the hot flues.

In all cases efficient ventilation is secured by means of numerous side windows, which can be readily opened and closed at will.

10*th Operation. Steeping.*—Run the cloth in the open width through a machine consisting of a large vat divided into several compartments fitted with rollers above and below. The first compartments are filled with a solution of carbonate of soda at $\frac{1}{2}$° Tw. (Sp. Gr. 1·0025), and heated to 40° C. The last is filled with water only.

The cloth is then well washed, and dried in the stove at about 65° C.

11*th to* 14*th Operation.*—These operations, consisting of *mordanting*, *dyeing*, and *clearing*, are precisely similar to those already described for yarn-dyeing.

It may be well to state that the number of paddings in dilute soda solution (liquoring) varies according to the quantity of oil which it is desired to fix upon the cloth. Good Turkey-red contains about 10 per cent. of modified oil on the fibre.

402. "Sulphated Oil Process" for Dyeing 500 kilos. of Yarn or Cloth.—In this process the frequent repetitions of passing the fabric through oil-emulsions or sodium carbonate and then stoving are not used. The olive oil is replaced by an alkaline solution of sulphated olive or castor oil (*see* p. 234) with which only a single impregnation is necessary, followed by a steaming or stoving process.

1*st Operation. Bleaching* or *Boiling.*—This is identical with that already given in describing the previous processes for yarn and cloth.

2*nd Operation. Preparing.* — The dry cotton is thoroughly impregnated by "tramping" or "padding" with a cold or tepid solution of 10—15 kilos. of neutralised sulphated-oil (50 per cent.) per 100 litres of water. The excess is removed, and the cotton is merely dried in the stove, or it may be heated for 1—2 hours to 75° C.

3*rd Operation. Steaming.*—The prepared and dried cotton is submitted to the action of steam, 2—5 lb. pressure, during 1—1½ hour.

4*th Operation. Mordanting.*—The cotton is worked and steeped for 2—4 hours in a tepid solution of commercial aluminium acetate (tin-red-liquor), or more economically in basic aluminium sulphate, $Al_2(SO_4)_2(OH)_2$, at 8° Tw. (Sp. Gr. 1·04).

After mordanting, the excess of aluminium solution is removed by wringing or hydro-extracting, the cotton is dried and then either simply well washed in cold water, or first worked for half an hour at 40°—50° C. in a chalk bath containing 20—30 grams of ground chalk per litre. A solution of sodium phosphate may replace the chalk water. Alkaline fixing-agents like ammonia and sodium carbonate are best avoided in case any of the oil-preparation should be stripped off.

5*th Operation. Dyeing.* — Dye with 15—20 per cent. of Alizarin (10 per cent.), with the addition of 1 per cent. of its weight, of chalk or acetate of lime. The cotton is dyed in the cold for half an hour to ensure regularity of colour, the temperature is then gradually raised to 70° C. in the course of an hour, and the dyeing is continued at this temperature till the bath is exhausted.

The cotton is then well washed (although with highly calcareous water this is best omitted), hydro-extracted, and dried.

6th Operation. Second Preparing.—The dyed and dried cotton is again impregnated with a dilute solution of neutralised sulphated oil (namely, 50—60 grams of sulphated oil [50 per cent.] per litre), and then dried. This second preparing may also take place after the mordanting, the oil being then fixed by means of a second mordanting with a weak solution of basic aluminium sulphate, &c.

7th Operation. Second Steaming.—The dried cotton is steamed as before, for one hour.

8th and 9th Operations. First and Second Clearing.—These may be identical with operations 13 and 14, described in the "Emulsion process," although many chemists think that soap alone should be used here, and consider that the addition of stannous chloride is altogether unnecessary if not irrational.

The "sulphated-oil process" is comparatively so new, that numerous slight modifications of the process as here given are naturally tried and adopted by various dyers, and to some of these reference will now be made.

The sulphated-oil used is invariably carefully neutralised, either with caustic soda or ammonia. As a rule, ammonia is preferred, since even the addition of an excess of ammonia would have little or no injurious effect, owing to its volatility; and further, the ammonia compound of sulphated-oil is more readily decomposed on steaming than the sodium compound, and a more complete fixing of the oil results. Either sulphated castor oil or olive oil may be used. Very good results are even obtained by the simple use of a carefully made castor oil soap, which, being excessively soluble, and giving thin solutions, is well fitted to impregnate the fibre thoroughly.

In the "preparing" process, the cotton does not attract or fix any of the oil. It simply absorbs a definite

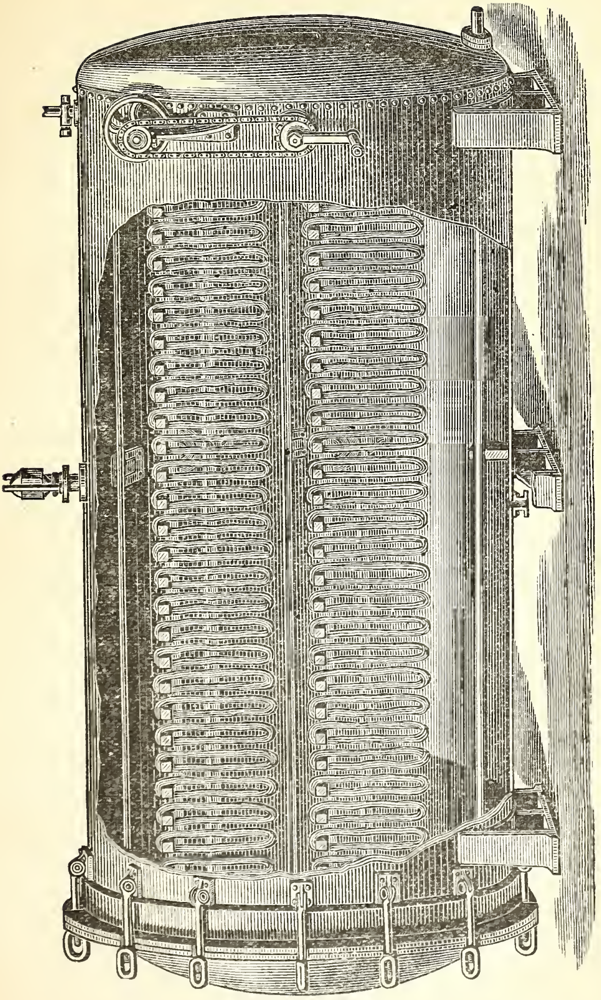


Fig. 94.—Steaming-Chest for Turkey-red Yarn.

amount of the solution, and supposing sulphated *olive oil* to have been used, the prepared cotton contains the sodium or ammonium compounds of oxyoleïc acid and of the glycerine-sulphuric-ethers of oxyoleïc and oxystearic acids, these being its constituent elements. It is very important to know the exact percentage of sulphated-oil contained in the solution, since it is this which determines the amount of oil and alumina ultimately fixed on the cotton, and consequently the beauty, brilliancy, and fastness of the colour.

According to Liechti and Suida, the action of the *first* steaming process is, to decompose the ammonium or sodium compounds of the ether constituent of sulphated-oil into ammonium or sodium sulphate, glycerine, oxyoleïc and oxystearic or trioxyoleïc acid, according as olive or castor oil has been employed. The other constituent (oxyoleïc or trioxyoleïc acid) remains unchanged. At the same time the steaming causes a better penetration of the fibre by these oxidised fatty acids. Sometimes the steaming at this stage is altogether omitted. The decomposition of the compound ether referred to may also be effected by heating the dye-bath to the boiling point instead of only to 70° C., the bath becomes acid, and the brilliancy of the colour is developed suddenly.

Fig. 94 represents a steaming-chest for yarn made by Messrs. Tulpin Frères, of Rouen. The hanks of cotton are suspended on square wooden rods resting on an iron skeleton-carriage or framework, and are capable of being turned during the steaming process to ensure every portion being efficiently steamed. The iron carriage is supported on wheels, so that it can be filled with yarn and then run into the chest. The steaming-chest itself consists of a wrought-iron horizontal boiler, with a movable door at one end provided with clamps. For the prevention of drops there is fixed internally and at the top a cover of sheet-copper, in such a manner as to leave a space between it and the boiler-plate. The chest is provided with a steam-gauge, safety-valve, and blow-off

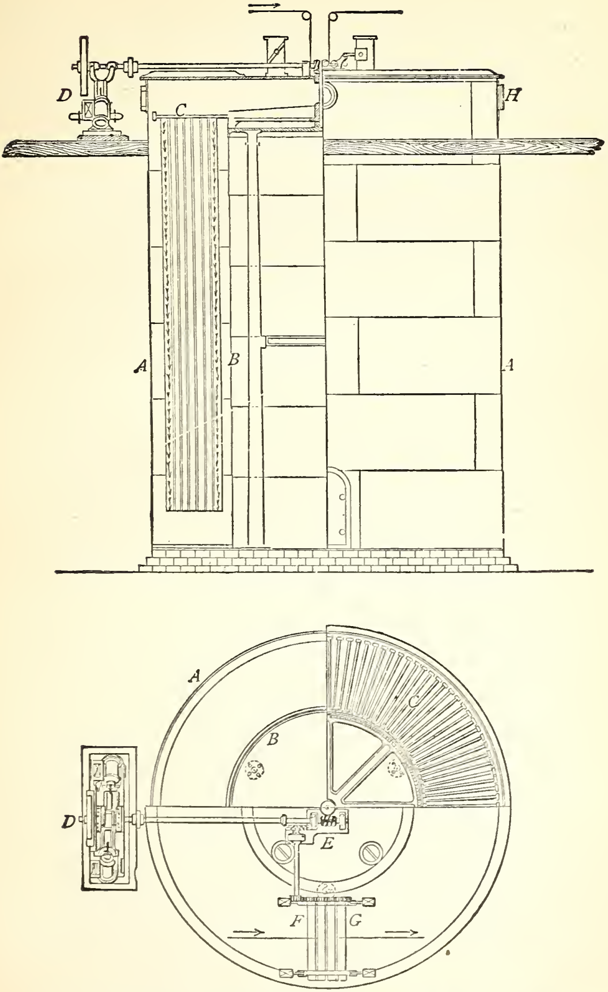


Fig. 95.—Plan and Elevation of Continuous Steaming-Chest.

pipe. The steam enters by a perforated pipe running along the bottom of the boiler, and which is usually covered with a perforated iron plate.

Cotton cloth may be reeled and suspended on rods in a similar way, or it may be steamed in the continuous steaming-chest of Messrs. Duncan Stewart and Co., Glasgow, represented in Fig. 95. It consists of an annular-shaped iron cylinder or chamber A B, in the upper part of which a series of brass radial rods C are caused to circulate slowly by means of the endless screw E driven by the engine D. The cloth (in the open width) enters the annular space through a pair of squeezing rollers at F. By an ingenious arrangement the cloth is suspended in long, loosely-hanging folds on the radial rods, is carried round the annular space, and makes its exit by a second pair of squeezing rollers at G. The chamber is constructed of boiler-plate, so that the goods can be submitted to high-pressure steam. Another form of continuous steaming-machine is that in which loose rods, supporting the cloth in a similar manner, are passed continuously by means of endless chains through a large rectangular brick chamber filled with very low-pressure steam.

If in the mordanting process the cotton was merely dried after the preparing with sulphated-oil, there are produced upon the fibre the aluminium compounds both of the ether and of the oxy- or trioxy-oleïc acid; but if it was also steamed, there is then fixed on the fibre essentially the normal aluminium compound of oxy- or trioxy-oleïc acid (Liechti & Suida).

A brighter colour is obtained by adding a small proportion of stannous chloride to the aluminium solution, or stannate of soda to the oil solution.

After mordanting and washing, a slightly basic aluminium salt remains on the fibre, its basic character being generally caused by the calcareous condition of the water. Traces of lime are also present. If, previous to washing, a warm chalk bath is used, a much more basic and more calcareous aluminium compound is formed.

During the dyeing process there is probably formed the Alizarin compound of the basic oxy- or trioxy-oleate of aluminium and calcium just referred to.

If there is a deficiency of oil on the fibre, the brightest shades are always obtained by dyeing at the low temperature indicated (70° C.), but otherwise the temperature may be raised to the boiling point, although there is then a tendency of a portion of the oily mordant being softened and boiled out, especially if it is in slight excess.

With the use of pure Alizarin—*i.e.*, the "blue shade of Alizarin," as it is generally called—a fiery brilliant red is not obtained; hence such as contains Isopurpurin (Anthrapurpurin)—*i.e.*, the "yellow shade of Alizarin"—is generally preferred.

The second preparing and steaming operations have for their object the neutralising of the basic compound present on the fibre at this stage. This operation of steaming after dyeing has a most remarkable effect in giving brilliancy and fastness to the colour, especially if the dyeing has been conducted at a low temperature. If 100° C. was employed, then the brightening effect has taken place to a considerable extent, if not entirely, already in the dye-bath, as above mentioned. Sometimes the second preparing is omitted, and a small quantity of neutralised sulphated-oil is added to the dye-bath instead.

The method of "clearing" described (*see* p. 434), in which the cotton remains stationary while the liquor circulates through it, gives very much better results than if the cotton were worked vigorously in the solution, since in this latter case much of the red-lake would be mechanically removed by friction, and the colour would look poor and weak.

403. **The Action of Lime-salts in the Dye-bath.**—One of the most interesting facts connected with the

application of Alizarin, is the necessity of the presence of a lime salt in the dye-bath, in order to obtain a really good serviceable colour. The general result of researches made by Schlumberger, Rosenstiehl, and others, with a view to elucidate this point, seems to favour the idea that the Alizarin-red-lake, as fixed upon textile fibres, is not simply an aluminium compound of Alizarin, but one which also contains calcium as an essential constituent.

The following results of Liechti and Suida's researches bearing on this point will explain this. Pure aluminium hydrate, whether in its precipitated form or fixed on the fibre, cannot be properly dyed with Alizarin except in the presence of lime compounds. Normal aluminium phosphate behaves similarly. Normal aluminium alizarate [$Al_2(C_{14}H_6O_4)_3$] is a purplish-red compound soluble in water, alcohol, and ammonia. Basic aluminium alizarates—*e.g.* [$Al_2(C_{14}H_6O_4)(OH)_4$] and [$Al_4(C_{14}H_6O_4)(OH)_{10}$]—are, on the contrary, bright red compounds, insoluble in water and alcohol, and little soluble in ammonia. Aluminium-calcium-alizarates of very varied composition, prepared by dyeing aluminium hydrate with Alizarin in the presence of calcium acetate, are mostly reddish-brown insoluble compounds. The amount of lime-salt present in the dye-bath determines the quantity of Alizarin which will be taken up by the alumina, and the amount of lime taken up by the lake is determined by the quantity of Alizarin employed. The relative proportions of Alizarin, alumina, lime, and fatty acid present in the lake abstracted from Turkey-red and Alizarin-red-dyed cotton, vary considerably, according to the method of dyeing employed; as a rule, a large excess of alumina, in proportion to the lime and Alizarin, is present. The above-mentioned authors find that alumina-mordanted cotton, when dyed with Alizarin in the presence of calcium acetate, takes up $\frac{1}{3}$ molecule of lime for each molecule of Alizarin, and they consider that the composition of the lake in unsoaped Alizarin-red-dyed cotton is best expressed by the formula $[Al_2Ca(C_{14}H_6O_4)_3(OH)_2]$.

404. Another Method of Dyeing Alizarin Red on cotton, in use among calico-printers, but which does not give quite such fast colours as those described above, is given in the following *résumé*:—

1. Mordant with commercial aluminium acetate, 5°—8° Tw. (Sp. Gr. 1·025 — 1·04), dry, and age for 1—2 days, by hanging in a chamber heated to 50° C., and having a somewhat moist atmosphere.

During this "ageing" process much of the acetic acid escapes, and alumina or a basic aluminium acetate is fixed on the fibre.

2. In order to fix the alumina more completely, work the cotton for a few minutes at 60° C. in a bath of phosphate, arsenate, or silicate of soda, 5—10 grams per litre; then wash well in water.

3. Dye with Alizarin, and dry. A small addition of acetate of lime is used if necessary. Since the cotton at this stage contains no oil, it is essential to the obtaining of a bright colour, that the dyeing should take place at a temperature not exceeding 70°—75° C.

4. Prepare with a neutralised solution of sulphated-oil, 50—100 grams (50 per cent.) per litre, and dry.

5. Steam for $\frac{1}{2}$—$\frac{3}{4}$ hour, at 2lb. pressure.

6. Clear as before.

405. Alizarin Pinks, Purples, &c., on Cotton.—Alizarin *pinks* are obtained by precisely the same methods as are adopted for reds. The aluminium mordant employed must, however, be considerably weaker—use, say, aluminium acetate at 10° Tw. (Sp. Gr. 1·05). Basic mordants are avoided, since they give uneven colours, and even normal aluminium sulphate may be used with advantage; the amount of Alizarin (20 per cent.) may be reduced to about 1 per cent. of the weight of cotton, and the proportion of oil-preparation required is correspondingly diminished. The most pleasing pinks are those produced by using a "blue shade of

Alizarin," *i.e.*, one free from Isopurpurin, Flavopurpurin, or Purpurin.

Very good fast shades of *purple* and *lilac* are obtained from Alizarin, either with or without the use of oil-preparation; indeed, the use of oil does not seem to add any particular brilliancy to the colour, but serves mainly to fix the mordant, and to make the colour a little faster to boiling soap solutions.

When the cotton is prepared with oil, according to either the Emulsion or Steiner's process for Turkey-red, it is mordanted, worked and steeped for a short time in a solution of ferrous sulphate at 3°—4° Tw. (Sp. Gr. 1·015—1·02); it is then allowed to lie overnight, and is finally well washed.

The amount of iron precipitated on the fibre, and of Alizarin subsequently taken up in the dye-bath, is determined by the amount of oil previously fixed, and not merely by the concentration of the ferrous sulphate solution. For the darker shades of purple, therefore, the cotton should be well prepared with oil, while for pale shades the preparation is slight. The best and bluest shades are only obtained when the mordant is thoroughly saturated with Alizarin, any excess of uncombined mordant gives the colour an unpleasant dull-reddish appearance.

The use of pyrolignite of iron gives somewhat darker, brighter, and bluer shades than the sulphate. Very deep purplish blacks are obtained, and with less oil-preparation, by steeping the cotton, previous to mordanting, in an infusion of gall nuts, or other tannin matter.

After mordanting, the cotton is well washed and dyed with 5—15 per cent. of Alizarin (10 per cent.). If the water is not sufficiently calcareous, it is very essential to add the necessary quantity of chalk or acetate of lime to the dye-bath (1—2 per cent.). After dyeing, the cotton should be washed and soaped at a temperature of 60° C.

When not prepared with oil, the cotton is prepared with tannin, by working it in a cold infusion of tannin matter (equal to 1—2 grams of tannic acid per litre); it is then mordanted in a solution of pyrolignite of iron 1°—3° Tw. (Sp. Gr. 1·005—1·015), and finally washed.

One may also mordant the cotton by impregnating it with pyrolignite of iron, 1°—3° Tw., wringing out the excess, and then working it for ten minutes at 50° C., in a solution containing 20 cubic centimetres of silicate of soda 16° Tw. (Sp. Gr. 1·08) per litre, and finally washing it. Anthrapurpurin gives greyish violets, Flavopurpurin and Purpurin reddish violets, which are little esteemed.

Various shades of *chocolate*, *claret-red*, &c., are obtained with Alizarin, by mordanting the oil-prepared cotton with a mixture of aluminium and iron mordants, either in the state of sulphates or acetates. Whether the cotton is prepared with oil according to the Emulsion or Steiner's process, or by the Sulphated-oil method, it is advisable to work it in a weak tannin bath before mordanting, especially for the darker and bluer shades, since a better proportion of iron is fixed by this means.

The different shades are produced by varying the relative proportions of aluminium and iron mordant, remembering always to vary the concentration of the tannin bath in accordance with the latter.

After mordanting, the cotton is washed, dyed with Alizarin, prepared with weak sulphated-oil, steamed, and soaped, as already described.

Certain shades of claret-red may also be obtained by mordanting with a solution of chromium acetate, instead of with the mixture of iron and aluminium salts.

Although Alizarin and Anthrapurpurin have been mainly alluded to in the above, the other members of the anthracene group—namely, Flavopurpurin and Purpurin —may be applied in exactly the same way, and give rise to similar shades.

406. *Application to Wool.*—Alizarin is capable of yielding a number of pleasing shades on wool, according to the mordant used, and ought to be largely employed whenever fastness to milling and to light is required. In conjunction with other colouring matters which are

similarly applied, it may yield an endless variety of shades. Its application presents little or no difficulty.

To obtain Alizarin-red on wool, mordant the wool with 6—10 per cent. of *aluminium sulphate* (cake alum) and 5—8 per cent. of cream of tartar. Introduce the wool into the cold solution, raise the temperature gradually to the boiling point in one hour, and continue boiling $\frac{1}{4}$—$\frac{1}{2}$ hour. Wash well, and dye in a separate bath, with 10 per cent. of Alizarin (20 per cent.) and 4—6 per cent. of acetate of lime (solid). In order to ensure an even colour it is well to work the wool for half an hour in the cold dye liquor, then to raise the temperature gradually in the course of an hour to the boiling point, and boil a quarter of an hour, or till the bath is exhausted. After dyeing, wash well, and dry at a low temperature or in the open air.

The addition of cream of tartar to the mordanting bath is absolutely essential to the production of a full rich colour. Excess of tartar tends to give intensity, but diminishes the brilliancy of the colour. Care must be taken that the aluminium sulphate used is free from iron. With a deficiency of mordant the colour lacks brilliancy and intensity, and if the deficiency is excessive only a poor dull brick-red is obtained. With excess of mordant the colour tends to become yellower and less intense. Brighter and more orange shades are obtained by using, along with the aluminium sulphate, 1—4 per cent. of stannous chloride, in which case a further addition of 1—4 per cent. of cream of tartar is necessary.

The addition to the dye-bath of acetate of lime (or an equivalent amount of ground chalk) is also *absolutely* necessary if the water employed is not sufficiently calcareous. Without lime, the colour is poor and worthless, and the dye-bath is not exhausted; with excess, the red is darker and duller.

On comparing the colours given by the various members of the Alizarin family of colouring matters, it is found that Alizarin itself yields a very blue shade of red, or a claret-red; Anthrapurpurin, a bright red; Flavopurpurin, a somewhat duller and yellower red; Purpurin, a shade approaching that given by Alizarin, but much yellower, namely, a dull brownish-red.

To obtain Alizarin-orange on wool, mordant the wool with 5—8 per cent. of *stannous chloride* (tin-crystals) and an equal weight of cream of tartar. Dye with 10 per cent. of Alizarin (20 per cent.) without the addition of acetate of lime. With the addition of 4—5 per cent. of acetate of lime a bright orange-red is obtained, but without, the colour is very much yellower. Excess of lime makes the orange still redder, but it is apt to be uneven. Alizarin-orange may also be dyed in a single bath. Alizarin gives a bright reddish orange; Flavopurpurin a bright yellowish-orange. The colour yielded by Anthrapurpurin holds an intermediate place; it is a bright orange. Purpurin gives a moderately bright orange-red.

Very rich claret-brown shades are obtained by mordanting the wool with 3 per cent. of *bichromate of potash* and 1 per cent. of sulphuric acid 168° Tw. (Sp. Gr. 1·84). The addition of the sulphuric acid is beneficial, since it tends to give a somewhat yellower and fuller colour; it is not, however, absolutely essential. Dye with 10 per cent. of Alizarin (20 per cent.). The addition of 2—4 per cent. of acetate of lime to the dye-bath makes the colour somewhat less yellow, or bluer, though apparently slightly less intense. Strange to say, its addition is by no means essential, as in the case of the aluminium mordant for dyeing reds. Good colours are also obtained by the single-bath method; use 1 per cent. $K_2Cr_2O_7$ and 1 per cent. H_2SO_4, 168° Tw. Numerous fast shades of brown, olive, purple, &c., are obtained by associating Alizarin with such colouring matters as Galleïn, Cœruleïn, and many of the dyewoods.

The shades yielded by the different members of the Alizarin group with chromium mordant are as follows: Alizarin gives a dull purple colour; Anthrapurpurin, a much redder shade, namely, a claret-brown; Flavopurpurin, a yellower shade of claret-brown; Purpurin gives the most intense colour of all, namely, a deep claret-brown.

Very good shades, ranging from bluish-violet to slate, are obtained by mordanting wool with 4—8 per cent. *ferrous sulphate* and 4—8 per cent. cream of tartar, and dyeing in a separate bath with 10 per cent. Alizarin (20 per cent.) and 5 per cent. carbonate of lime. With the single-bath method darker colours are obtained, but they are much browner and duller; use 6 per cent. ferrous sulphate and 0·6 per cent. oxalate of potash. Iron-alum employed instead of ferrous sulphate gives good results.

Copper sulphate as the mordant gives claret-browns, either by the mordanting and dyeing method or by the single-bath method.

With the use of *ammoniacal sulphate of nickel* and *uranium salts*, as mordants, Alizarin yields nice shades of grey and slate.

Application to Silk.—Alizarin is as yet little used in silk-dyeing. Good colours may be obtained by mordanting the silk according to the ordinary methods, and working it, after dyeing, in hot soap solution.

407. Nitro-Alizarin. [$C_{14}H_5{\cdot}NO_2{\cdot}(OH)_2$.]—This colouring matter, also called *Alizarin Orange*, is produced by the action of nitrous acid on Alizarin. It is applied to the various fibres in the same way as Alizarin; although it yields fast colours, it finds as yet only a comparatively limited employment.

Application to Wool.—With *aluminium mordant* it yields very good orange colours. Mordant the wool with 6—8 per cent. of aluminium sulphate and 7—9 per cent. of cream of tartar. Excess of mordant renders the shade dull. The addition of acetate of lime to the dye-bath makes the colour browner.

With *stannous chloride* mordant the colour obtained varies very considerably, according to the amount of mordant employed. With a small amount (1 per cent. of stannous chloride and 1·5 per cent. of cream of tartar), a very reddish-orange is obtained; with double the amount, the colour becomes a yellowish-orange; with 4 per cent. of stannous chloride, only a dull brown is obtained, the normal colour being evidently destroyed by the reducing action of an excess of mordant. The addition of acetate of lime to the dye-bath is not beneficial, since the yellowish-orange colour is thereby changed to brown.

With *stannic chloride* (equivalent to 6 per cent. stannous chloride, $SnCl_2 \cdot 2H_2O$) an orange colour is also obtained. Excess of mordant does not destroy the colour as in the case of stannous chloride.

With *copper sulphate* mordant a very good brownish-red is obtained. Use 4—6 per cent. of copper sulphate, without calcium acetate.

With *ferrous sulphate* as the mordant a purplish-brown is obtained. Use 6—8 per cent. of ferrous sulphate, without calcium acetate in the dye-bath.

Bichromate of potash as the mordant yields dull brownish-reds. Use 3 per cent. of potassium dichromate and 2 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). When potassium dichromate alone is employed, the colour becomes darker with increase of mordant, even till 16 per cent. be employed.

408. **Alizarin Blue** [$C_{17}H_9NO_4$]. — This colouring matter, also called Anthracene Blue, is derived from Nitro-alizarin by heating it with glycerine and sulphuric acid. It may be considered as the quinolin of alizarin, and has in consequence both basic and acid properties. It is met with in commerce in two forms, namely, as a paste containing about 10 per cent. of dry substance, and as a powder under the name of Alizarin Blue S. The former is insoluble in water, although certain commercial marks (WX, WR) possess some degree of solubility. The latter, which is, indeed, a sodium disulphite compound of Alizarin Blue ($C_{17}H_9NO_4 \cdot 2NaHSO_3$), is readily soluble in water, with a brownish-red colour. Its solutions decompose, if heated to 70° C., with precipitation of the insoluble form of blue. With lime it forms an insoluble compound; hence the presence of

lime salts in the dye-bath must be avoided, otherwise there will be a loss of colouring matter.

The insoluble form of Alizarin Blue may be applied in dyeing, according to the indigo-vat method, by reducing it with zinc powder and carbonate of soda, or by the ordinary method of mordanting and dyeing in separate baths. When the latter method is employed, a certain proportion of disulphite of soda may be added to the dye-bath to render it soluble, or the dyeing at 100° C. must be long continued. Avoid the use of copper dye-vessels.

With Alizarin Blue S the mordanting and dyeing method only is employed.

Application to Cotton.—Mordant the cotton with chromium according to the alkaline method. Dye in a separate bath with Alizarin Blue; raise the temperature gradually to the boiling point in the course of an hour and a half, and continue boiling for half an hour.

Application to Wool.—The most suitable mordant to employ is *bichromate of potash*, in the proportion of 3—6 per cent. of the weight of wool. The addition of sulphuric acid, 168° Tw. (Sp. Gr. 1·84), is not beneficial if used in larger amount than 1 per cent. Dye in a separate bath with Alizarin Blue; raise the temperature gradually to the boiling point, and continue boiling until a bright pure shade is obtained. With insufficient boiling the colouring matter is only superficially attached to the fibre. The colour obtained is a bright indigo-blue, with purplish bloom. It is exceedingly fast to scouring, milling, light, &c., and has the advantage of not rubbing off.

When *aluminium sulphate* is the mordant employed a purplish-blue is obtained, which is very liable to be uneven unless great care is taken. Use 6—8 per cent. of aluminium sulphate and 5—7 per cent. of cream of tartar.

With *stannous chloride* mordant a much redder purple is obtained. Use 4 per cent. of stannous chloride (crystals) and 2 per cent. of cream of tartar. This mordant is not suitable for employing alone.

Ferrous sulphate, as a mordant for Alizarin Blue, is also little suitable. It gives a greenish-blue colour, possessing little brilliancy, and apt to be uneven. Mordant with 4 per cent. ferrous sulphate and 8 per cent. cream of tartar.

Application to Silk.—Mordant the silk with aluminium or iron in the usual manner; wash and dye in a separate bath with Alizarin Blue. Brighten the colour afterwards by boiling the silk in a soap bath.

CHAPTER XXI.

ARTIFICIAL COLOURING MATTERS CONTAINING SULPHUR.

409. Cachou de Laval (Poirrier).—This dyestuff is produced by fusing sodium sulphide with waste vegetable or animal matter. Care should be taken to preserve it from becoming damp by exposure, otherwise it is deteriorated, becomes more or less insoluble, and dissolves with a brown colour. It is specially applicable to cotton, and yields various buff and grey colours, which are very fast to acids and alkalis, and fairly fast to light.

Application to Cotton.—Dissolve the dyestuff in boiling water. The normal colour of the solution is a deep bottle-green; if it is brown, add a little carbonate of soda, and boil for a short time. Avoid using calcareous water, either for solution or in the dye-bath, since this precipitates the colouring matter. If lime is present, acidify slightly with acetic acid. Add the colour solution to the dye-bath, also sodium sulphate in the proportion of 40—70 per cent. of the weight of Cachou de Laval.

Dye the cotton for about half an hour, at a temperature of 60° C., in a somewhat concentrated solution (100 grams per litre). Add the colour solution gradually. After dyeing, wash well, and work the cotton for 5—10 minutes, at 50° C., in a dilute solution of one or other of the following:—bichromate of potash, ferrous sulphate, copper sulphate, sulphuric acid, hydrochloric acid. Wash and dry. Cachou de Laval acts also as a mordant, so that various shades can be obtained by dyeing afterwards in solutions of basic coal-tar colouring matters.

Dyewood extracts may also be applied, since these are attracted by reason of the metallic oxide present in the finished Cachou colour.

410. Canarin ($C_3N_3S_3H$).—This yellow colouring matter is simply perthiocyanogen. It is produced as an insoluble powder when potassium thiocyanate (sulphocyanide of potassium) ($CN{\cdot}SK$) is oxidised by potassium chlorate in the presence of sulphuric and hydrochloric acid. It is dissolved by boiling it with a solution of borax (100 grams per litre). It is specially adapted for dyeing cotton, on which it gives bright yellow or orange shades extremely fast to light, alkalis, acids, and hypochlorites. It acts as a mordant for basic coal-tar colouring matters; hence pleasing compound shades may be obtained by applying these in a separate bath.

Application to Cotton.—Add to the dye-bath the necessary amount of borax Canarin solution and a small amount of soap. Introduce the cotton cold, and raise the temperature gradually to the boiling point. Rinse in cold water and dry.

The use of calcareous water in dyeing must be avoided.

Wool may be dyed in a similar manner.

APPLICATION OF THE MINERAL COLOURING MATTERS.

CHAPTER XXII.

CHROME YELLOW — IRON BUFF — MANGANESE BROWN — PRUSSIAN BLUE.

THE mineral colouring matters applied in dyeing are extremely limited, and they are almost entirely confined to the vegetable fibres, the most notable exception in this respect being Prussian Blue, and this, strictly speaking, is not a mineral colouring matter.

411. **Chrome Yellow.**—Reference has already been made to the production of this colour, in describing the application of bichromate of potash and of lead salts to the cotton fibre (*see* pp. 207, 225).

In addition to the methods there indicated, the following, specially intended for orange, may be used.

Prepare a bath of plumbate of lime by adding a solution of 15—25 kilos. of pyrolignite of lead to milk of lime containing 20—30 kilos. of lime, and 500 litres of water. The mixture is well agitated, and then allowed to settle for about two hours.

The cotton is worked, and steeped in the more or less milky supernatant liquid for 1—2 hours, then squeezed and washed. Dye in a cold or tepid (40°—50° C.) solution containing 5 per cent. of bichromate of potash, and $\frac{1}{2}$—1 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). Wash, and develop the orange colour by passing the cotton into clear, boiling, lime-water, then wash and dry. The cotton must be removed from the lime-water bath whenever the full orange colour is developed, otherwise the colour loses brilliancy.

412. **Iron Buff.**—This colour simply consists of

ferric oxide. It is produced by first impregnating the cotton with a ferrous salt solution, then passing it through an alkaline solution, to precipitate ferrous hydrate; the latter is then changed into ferric hydrate by simple exposure to the air, or, preferably, by passing the cotton into a cold dilute solution of bleaching-powder.

Instead of a ferrous salt, one may also employ a ferric salt, *e.g.*, ferric sulphate or nitrate. The cotton is simply impregnated with the ferric solution, then squeezed, and passed rapidly through a dilute solution of carbonate of soda, ammonia, or milk of lime. In this case, ferric hydrate is at once precipitated on the fibre, and no subsequent oxidation is necessary.

Iron Buffs are very fast to light and boiling alkaline solutions, but are sensitive to the action of acids.

413. **Manganese Brown.**—The production of this colour on cotton is briefly described on page 225; it is exactly analagous to the production of Iron Buff from ferrous salts. The process is simplified by adding a little sodium hypochlorite to a solution of caustic soda, passing the cotton impregnated with manganous chloride at once through this mixture. In this case, precipitation and oxidation take place simultaneously.

It is very important always to use caustic soda free from carbonate, otherwise a little manganous carbonate is precipitated on the fibre, and since this compound does not oxidise readily, the colour is apt to be irregular.

According to A. Endler, irregularity of colour may also arise from the unsuitable physical properties of the precipitate itself, when it is produced in the ordinary manner described. Endler obviates these defects by passing the cotton, after impregnation with manganous chloride, into a bath containing 25 litres of water, 7 litres of ammonia, and 500 grams of bichromate of potash. A somewhat unstable chromate of manganese is formed on the fibre, which, on decomposing, allows the chromic acid to react on the manganous hydrate and change it into some higher state of oxidation. A final passage in dilute bleaching-powder solution completes the process.

Manganese Brown is very fast to the action of light, alkalis, and acids.

414. **Prussian Blue.**—*Application to Cotton.*—Prussian Blue was formerly very much dyed upon cotton. Since the introduction of Aniline blues it has been much less employed.

The cotton is first dyed an Iron Buff, and is then dyed in a cold solution of potassium ferrocyanide, 20 grams per litre, with the addition of 10 grams of sulphuric acid, 168° Tw. (Sp. Gr. 1·84). Wash and dry. The intensity of the blue depends upon the quantity of ferric oxide fixed upon the fibre in dyeing the buff.

Fine purplish shades of blue are obtained by working the cotton at 30° C. in nitro-sulphate of iron at 5° Tw. (Sp. Gr. 1·025) to which 2—3 per cent. of stannous chloride has been added, and then dyeing in a cold acidified solution of potassium ferrocyanide. Wash and dry; or if a still more purplish tone of colour is required, work for a short time in a tepid bath containing Methyl Violet or Logwood liquor.

Alkaline or boiling soap solutions readily decompose Prussian Blue, leaving brown ferric oxide on the fibre. Prolonged exposure to sunlight causes the blue to fade, but it is restored if kept for some time in the dark.

Application to Wool.—Prussian Blues (sometimes also called Royal Blues) are obtained on wool by means of red and yellow prussiate of potash, *i.e.*, potassium ferri- and ferrocyanide. The former gives the best results.

The method depends upon the fact that when a mineral acid is added to solutions of either of these salts the corresponding hydro-ferri- or hydro-ferro-cyanic acids are liberated, and these, under the influence of heat, and by oxidation decompose and produce insoluble Prussian Blue. If, then, wool is boiled in an acidified solution of these salts, the liberated acids are taken up by the wool, decomposition takes place gradually, and Prussian Blue is precipitated, and becomes fixed on the wool.

The wool is introduced into a cold bath containing a solution of 10 per cent. of red prussiate of potash, and 20 per cent. of sulphuric acid at 168° Tw. (Sp. Gr. 1·84) ; the temperature is gradually raised in the course of an hour to 100° C., and this temperature is maintained for $\frac{1}{2}$—$\frac{3}{4}$ hour.

The colour is rendered brighter and more purplish by adding 1—2 per cent. of stannous chloride during the last half to three-quarters of an hour of the boiling.

Although sulphuric acid gives the best result, one may also use nitric or hydrochloric acid, in which case the shade of blue is modified slightly. Nitric acid, for example, makes the shade greener. It is very usual with dyers to employ a mixture of all three acids, especially when yellow prussiate of potash is employed. This mixture of acids, which is called "royal blue spirits," or merely "blue spirits," may vary slightly in composition with different dyers. A usual mixture is the following: 4 measures of sulphuric acid 168° Tw. (Sp. Gr. 1·84), 2 measures of hydrochloric acid 32° Tw. (Sp. Gr. 1·16), and 1—2 measures of nitric acid 64° Tw. (Sp. Gr. 1·32).

When yellow prussiate of potash is employed, the use of nitric acid gives the best result, probably by reason of its oxidising action. For 10 per cent. of yellow prussiate of potash use 8—12 per cent. of nitric acid 64° Tw.

Instead of stannous chloride in the crystalline state, the dyer generally uses it in solution, as "muriate of tin." It is often sold to the dyer as "finishing blue spirits," though under this name it generally contains a slight addition of sulphuric or oxalic acid, or both. These additions, however, are not essential.

Another method of dyeing Prussian Blue, but one now seldom employed, is the following :—

The wool is worked for two hours at 30° C., in a solution of ferric sulphate 2° Tw. (Sp. Gr. 1·01), containing 2—3 per cent. of stannous chloride, and 2—8 per cent. of cream of tartar. The material is then well washed, and worked for two to three hours at 80°—90° C., in a bath containing 1 per cent. of yellow prussiate of potash, and 4 per cent. of oxalic acid, or sulphuric acid, 168° Tw. (Sp. Gr. 1·84).

In the first bath there is fixed on the wool ferric oxide, which combines with the free hydro-ferrocyanic acid contained in the second bath. The depth of blue is regulated by the strength of the ferric sulphate solution, and the amount of yellow prussiate in the second bath should correspond to the amount of ferric oxide fixed upon the wool.

Application to Silk.—Prussian Blue is now seldom dyed on silk, except as a groundwork for black.

What was formerly known as Raymond's Blue was dyed as follows:—

Work the silk in basic ferric sulphate (nitrate of iron), 5° Tw. (Sp. Gr. 1·025), for a quarter of an hour, wring out, and let lie over-night. Wash well, and work for a quarter of an hour in a boiling soap bath containing about 10 per cent. of soap; wash, and dye at 40°—45° C., for $\frac{1}{4}$—$\frac{1}{2}$ hour in a fresh bath containing 9 per cent. of yellow prussiate of potash, and 12 per cent. of hydrochloric acid, 32° Tw. (Sp. Gr. 1·16), and finally wash well.

So-called "Napoleon's Blue" is a brighter blue, produced as follows:—

Work for half an hour in a cold bath containing 50 per cent. of basic ferric sulphate, 50° Tw. (Sp. Gr. 1·25), 10 per cent. of stannous chloride, and 5 per cent. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84); wring out, wash, and work for half an hour at 40° C., in a second bath containing 10 per cent. of yellow prussiate of potash, 2—5 per cent. of red prussiate of potash, and 12—15 per cent. sulphuric acid, 168° Tw. (Sp. Gr. 1·84). After wringing out from this second bath, the whole process is repeated. Previous to drying, the silk is softened and brightened by working it for half an hour in a cold bath containing an imperfectly made sulphated-oil. For one kilo. of silk, use a mixture of 150 grams of olive oil and 15 grams. of sulphuric acid, 168° Tw. (Sp. Gr. 1·84).

THE DYEING OF MIXED FABRICS

CHAPTER XXIII.

FABRICS OF COTTON AND WOOL.

415. Mixed fabrics, or unions, may be of the most varied character. The wool and cotton may be intermingled throughout the whole fabric; or, what is more usually the case, each fibre may be confined to separate threads, forming either weft or warp.

One large class, comprising Cashmeres, Coburgs, Sicilians, Alpacas, Delaines, &c., are thin, light materials, generally used for ladies' wear. These consist of cotton warp and woollen or worsted weft, and may well serve for illustrating the general methods employed in dyeing mixed fabrics.

Such goods are made in two ways :—

1. The cotton warp may be dyed black, brown, dark blue, drab, &c., *before weaving*, in which case only the woollen or worsted weft is dyed subsequently. The finished goods are then said to be "cross-dyed."

2. When only light shades are required, the cotton and wool are always woven together in the undyed state, and are then "dyed in the grey." Dark shades are also dyed on this cloth.

Cross-dyeing is always preferred for medium and better class goods, since it is then possible to dye both the cotton and the wool with a greater choice of colouring matter and process, and the most suitable for each fibre may be employed. The cotton warps, for example, may then be dyed with such colours as will withstand the action of acids, so that acid-colours may be used in dyeing the wool.

Brighter colours, too, can be dyed on the wool because they are not subsequently soiled by the mordanting and dyeing operations otherwise necessary for the cotton. Further, it is remarked that cross-dyed goods have a much softer and more agreeable "feel" or "handle" than those dyed from the grey.

The general series of operations to which the materials are subjected in dyeing from the grey may be enumerated as follows: wetting, scouring and crabbing, steaming, drying, singeing, wetting, dyeing the wool, washing, dyeing the cotton, washing, drying, finishing. In practice, slight deviations are made to suit particular goods, or to obtain special effects.

Most of the operations have been already described (*see* pp. 76, 109, 286), and it may suffice here to discuss the dyeing.

416. Dyeing of Union Goods.—For light and medium colours the *wool* is dyed *first*, according to the methods usual for wool, in the machine illustrated on p. 283. Care should always be taken to keep the shade a little lighter than that ultimately required, since the wool invariably acquires a little colour during the subsequent dyeing of the cotton. After washing, squeezing, and opening out the cloth, the dyeing of the cotton warp is proceeded with.

The dyeing of the cotton usually requires three distinct operations, namely, impregnation of the fibre, first with tannic acid, secondly with nitrate of iron, stannic chloride, or tartar emetic, and thirdly with the solution of colouring matter. In order to influence the colour of the dyed wool as little as possible, all these operations are conducted in the cold. The machine employed and the mode of procedure are given on p. 262.

In plain colours, much judgment and practice is required on the part of the dyer to make the colour of the cotton and of the wool as identical as possible in tone and intensity.

Sometimes—*e.g.*, in the production of "shots," "figured damasks," &c.—it may be necessary, however, to dye totally distinct colours on the two fibres (*e.g.*, red and green), and produce an effect like that obtained if the weft and warp had been separately dyed before weaving. Since the introduction of the coal-tar colours, such effects can be obtained with ease, since it is only necessary to choose an acid-colour for the wool and a basic-colour for the cotton.

Heavy woollen goods containing cotton warp, are dyed by methods similar to those adopted for *thin* materials; but since the quality and thickness of the cloth render it unnecessary to keep it free from creases, as in the former case, the cotton is dyed in the ordinary winch dyeing machine, instead of in the jigger.

Even in dyeing ordinary all-wool goods, it is frequently necessary to employ the methods adopted for unions, in order to cover or dye the minute white or grey specks of vegetable fibres appearing on the face of the cloth, and arising from the presence of seeds, "burrs," &c., in the wool used. The operation of treating such goods with tannin matter and nitrate of iron is technically termed "burl dyeing."

The following brief notes will serve to give some idea of the methods adopted in dyeing various plain colours on unions.

417. Scarlet.—Various methods may be adopted.

1. Dye the wool a bright scarlet, with Cochineal and Flavin, according to the method usual for wool, making the shade a little yellower and paler than required, since in dyeing the cotton subsequently the wool acquires a bluer and deeper shade. Wash and dye the cotton as follows: pass the pieces for one hour through a cold infusion of Sumach, then for 1—1½ hour through a solution of stannic chloride at 3° Tw. (Sp. Gr. 1·015). Wash and dye the cotton yellow in a cold decoction of Quercitron Bark, then wash and dye in a cold decoction of Peachwood, until the proper shade is obtained.

2. Dye the wool in the usual way with one of the

Azo Scarlets, wash, and dye the cotton with a cold solution of Croceïn Scarlet and alum. The cotton may also be dyed by preparing it with Sumach and tartar emetic, and dyeing with a mixture of Safranine and Auramine.

3. A third method would be to dye the cotton and wool in one bath by means of Congo Red or Benzopurpurin.

418. **Yellow.**—Dye the wool with Flavin, stannous chloride, and tartar, or with a coal-tar Acid-Yellow; wash, and dye the cotton. Prepare it first with tannic acid, then with tartar emetic; wash and dye in a cold solution of Flavaniline or Auramine.

419. **Orange.**—Orange is dyed in the same manner as yellow, but a little Cochineal is added along with the Flavin, or one may use one of the acid Azo Oranges to dye the wool. For the cotton, a little Safranine must be used in addition to the Flavaniline or Auramine.

420. **Green.**—1. Dye the wool first with Old Fustic, Turmeric, Indigo Extract, alum, and tartar.

Dye the cotton by padding the pieces once or twice in nitrate of iron, 3° Tw. (Sp. Gr. 1·015). then wash, and pad in a cold solution of yellow prussiate of potash. When the cloth is uniformly impregnated with it, acidify the solution with sulphuric acid, and pad the cloth in the solution again. The cotton will thus be dyed Prussian Blue, and this is changed to green by padding in a cold decoction of Old Fustic, to which has been added acetate of alumina (red liquor). Wash slightly and dry.

Another method is the following:

2. Dye the wool in a neutral bath with Malachite Green, or in an acid bath with an Acid Green, and wash.

Mordant the cotton with tannic acid, then with stannic chloride or tartar emetic, and wash. Dye the cotton in a cold solution of Malachite Green.

If yellow shades of green are required, add Auramine in the requisite quantity.

421. **Blue.**—1. *Light Blue.*—Dye the wool a pale blue with Indigo Extract, alum, and tartar, and wash. Dye the cotton cold in two baths: (1) a weak solution of

nitrate of iron; (2) a dilute solution of yellow prussiate of potash, acidified with sulphuric acid.

2. *Royal Blue.*—Mordant the cotton by padding the pieces in nitrate of iron 4° Tw. (Sp. Gr. 1·02), then in carbonate of soda (4°—6° Tw.), and washing in water. These operations may be repeated two or three times, according to the shade of blue required.

Dye both the cotton and the wool in a solution containing yellow prussiate of potash and sulphuric acid 168° Tw. (Sp. Gr. 1·84) (10 per cent. of the weight of cloth of each). Enter the cloth cold, and raise the temperature gradually to the boiling point in the course of 1—1½ hour. During the last half-hour add a small quantity of stannous chloride to brighten the colour. Should the colour of the cotton suffer during the dyeing of the wool, and become too pale, it can be readily restored by working again in weak nitrate of iron, and in an acidified solution of yellow prussiate of potash.

Another method of dying Royal Blue is, to dye the wool first with an acidified solution of yellow prussiate of potash, in the manner already given, and wash. The cotton is then dyed a Logwood purple by working the goods for a short time in a cold, weak infusion of Sumach, then in a solution of muriate of tin 2° Tw. (Sp. Gr. 1·01) for half an hour. Wash and dye in a cold weak decoction of Logwood. Without washing, the cloth is then padded in weak nitrate of iron, and after being well washed, the cotton is dyed blue, by first working in a cold solution of yellow prussiate of potash without acid, then acidifying suitably with sulphuric acid, and working the cloth in it until the blue is properly developed.

3. *Aniline Blue.*—Dye the wool first with Alkali Blue, and wash.

Dye the cotton Prussian Blue by padding first in a weak solution of nitrate of iron, washing, and dyeing in an acidified solution of yellow prussiate of potash.

The cotton may also be dyed with aniline blue by working the cloth first in a solution of tannic acid, and then in tartar emetic, and dye with Night Blue, Methylene Blue, or Soluble Blue acidified by the addition of alum or sulphuric acid.

422. **Purple.**—Dye the wool first, according to the usual method, with Methyl Violet or Acid Violet, and wash well.

Mordant the cotton with tannic acid and tartar emetic, wash, and dye cold with Methyl Violet.

423. **Brown.**—Mordant the cotton in a cold infusion of Sumach, then in dilute nitrate of iron, and lastly in dilute stannic chloride. After washing well, dye the cotton and the wool together with a decoction of Peachwood, Logwood, Turmeric, in suitable proportions, to which has been added a certain amount of alum and copper sulphate. Dye at a temperature of 80°—100° C.

Browns are also frequently dyed by employing mixtures of suitable coal-tar colours.

424. **Drabs, Greys, &c.**—The wool is dyed first, according to the usual methods, with decoctions of Peachwood, Old Fustic, and Indigo Extract, in suitable proportions, to which have been added alum and tartar. As a rule, it is best to dye the cotton slightly darker than the wool, for if it is in the least under-dyed, the cloth has a mottled appearance.

The cotton is dyed by first padding it in a cold decoction of Sumach, and afterwards in nitrate of iron. The strength of both these solutions varies according to the depth of shade required.

It is impossible to give the precise amounts of each ingredient to be employed, so much depends upon the exact tint to be obtained.

425. **Black.**—Mordant the cotton by working it for 2—3 hours in a cold infusion of tannin matter, then for about one hour in nitrate of iron 4° Tw. (Sp. Gr. 1·02), and wash well.

Mordant the wool by boiling ½—1 hour with 2—3 per cent. of bichromate of potash, and wash. Dye the cotton and the wool simultaneously by boiling with Logwood and Old Fustic.

426. The dyeing of mixed fabrics of *cotton* and *silk*, and *wool* and *silk*, is of comparatively little importance. It is met with rather as a speciality than as a prominent branch of dyeing. It does occur, however, *e.g.*, in the dying of Barège, Grenadine (silk and wool), umbrella cloths (silk, wool, and cotton), &c., and perhaps most of all in the re-dyeing of worn articles of clothing (job-dyeing). Fabrics of cotton and silk would be treated somewhat like those of cotton and wool, while those consisting of wool and silk would present less difficulty, since the behaviour of these two fibres towards colouring matters is more or less similar, and a modification of methods suitable either for wool or silk might be adopted.

EXPERIMENTAL DYEING.

CHAPTER XXIV.

METHOD OF DEVISING EXPERIMENTS IN DYEING.

427. Experiments with Catechu. — In the present chapter it is intended to give some idea of the manner in which the intelligent textile colourist proceeds, in order to discover the best methods of applying colouring matters to textile fibres.

As an interesting example, the fixing of Catechu on cotton may be taken :—

First of all, the solubility of the colouring matter in ordinary solvents should be determined, *e.g.*, in water, acetic acid, alkalis, &c. The behaviour of the solutions towards ordinary practically useful reagents should then be ascertained.

An aqueous solution of Catechu thus tested would, for example, show the following properties :—

Gelatin gives a voluminous reddish-coloured precipitate.

Alkalis give the solution a brownish coloration.

Lime-water gives a yellowish coloration, and a precipitate.

Aluminium salts cause the solution to become lighter-coloured and yellowish.

Ferrous salts impart an olive-green coloration.

Ferric salts impart a dark-green coloration.

Copper sulphate gives an olive coloration.

Copper acetate gives a copious dark-brown precipitate.

Lead salts give a yellowish-grey precipitate.

Potassium dichromate gives a copious brown precipitate; &c. &c.

If a piece of calico is impregnated with an aqueous solution of Catechu, then dried, and at once washed, most of the colouring matter will be removed; if, however, previous to washing, it is allowed to hang for a lengthened period, or, better still, if it is steamed, it will be observed that a portion of the colouring matter will become oxidised and thus fixed on the fibre. This takes place still more largely if a weak alkaline solution of Catechu be employed, or if some oxidising agents—*e.g.*, certain copper salts—be added to the aqueous solution. The best results, however, are obtained by passing the steamed calico through a solution of potassium dichromate, a fact which was already indicated by the result obtained in the last-mentioned of the examinations in the test-tube. Greenish tones of colour are obtained by passing the cloth afterwards into iron solutions, or by padding the white calico in an acetic acid solution of Catechu containing ferrous sulphate, drying, and steaming. If in this last case the steamed calico be further passed into potassium dichromate solution, the colour is greatly developed in intensity, and becomes browner.

From the foregoing preliminary experiments, the method of applying Catechu to calico might be formulated as follows: Pad the cotton in an aqueous, alkaline, or acetic acid solution of Catechu, dry, age, steam, pass through a solution of potassium dichromate, and wash, *i.e.*, if brown tones of colour are required. For obtaining greenish tones, the method to be adopted would be to pass the calico, after steaming, through iron solutions, or to add ferrous sulphate to the padding solution.

But, however interesting the observations just recorded may be, only a very small portion of the problem has thus been solved; the question still remains, what relative and absolute proportions of the various ingredients should be employed, in order to obtain the most satisfactory result? Further, what are the best conditions under which the several substances must be applied, as regards temperature of solutions, duration of steeping, steaming, exposure to air, &c.

To answer these questions, another series of experiments is necessary. Several solutions are made, containing 25, 50, 100 grams of Catechu per litre of hot water, in each of which a "swatch," "fent," or "sample" of calico of suitable size is padded, then dried, and steamed. In a similar manner several solutions of potassium dichromate are made, containing, *e.g.*, 5, 10, 20 grams of $K_2Cr_2O_7$ per litre, and portions of each padded sample are passed into each dichromate solution, for, say, two minutes at the ordinary temperature. Similar portions are passed through identical solutions at a medium temperature, say, 50° C., and others again at the boiling point.

The experiments can be further extended by substituting alkaline chromate solutions for the potassium dichromate, or by adding varying quantities of some iron salt—*e.g.*, ferrous sulphate—to the Catechu solution before padding, and then passing the cloth, as before, through acid or alkaline chromate solutions. Experiments may also be instituted to determine the best mode of applying other colouring matters in conjunction with Catechu, in order to obtain various shades of colour, &c.

428. **Experiments with Tannic Acid.**—On adding a solution of tartar emetic to a solution of tannic acid (especially if ammonium chloride be added), a voluminous white precipitate is obtained, which, on experiment, is found to possess the power of attracting most of the coal-tar colouring matters of a basic character from their solutions, and combining with them to form colour-lakes, insoluble even in soap solutions. With these premises, let it be supposed that it is the object of the dyer to determine by a series of experiments what are the most favourable conditions for producing these colour-lakes upon the cotton fibre.

The method of procedure would be, first of all, to prepare several tannin solutions of different degrees of concentration, containing, for example, 2·5, 5, 10, 15, 20, 25 grams of technically pure tannic acid per litre. In each of these solutions a piece of calico should be steeped for a definite period, say six hours, and after removing excess of liquid by squeezing, &c., each piece should be divided into three portions. One portion of each might be passed *at once*—*i.e.*, in its *moist* condition—into a solution of tartar emetic; a second portion might be first *dried;* and a third portion might be *dried* and *steamed* previously. All the "swatches" might be immersed together in the same bath, if only one is assured that there is excess of tartar emetic present. After a quarter of an hour's immersion they should be thoroughly washed, to remove all loosely adhering precipitate, and then passed into a solution of some basic coal-tar colouring matter—*e.g.*, Methylene Blue.

The swatches are kept constantly stirred during immersion, and are thus dyed in the cold for about half an hour; from time to time further slight additions of colour solution are made; the bath is then gradually heated to about 60° C., and the swatches are allowed to remain in the solution until they have acquired the maximum intensity.

They are now taken out and well washed, and each swatch is divided into two parts. One half is dried, the other is worked for about a quarter of an hour in a soap-bath, heated to say 60° C., then rinsed in water and dried. Of course, each separate swatch is marked by holes cut near the edge, in order to distinguish it from the rest, and eventually they should all be pasted in a pattern book, and references to each should be written at the side.

If all the different coloured swatches are then carefully compared with each other, the following determinations may be made:—

1. The amount of tannic acid necessary to employ for obtaining a definite shade of blue.

2. The beneficial effect produced by drying or steaming of the tannin-prepared cotton is quantitatively determined, and it is at once seen how defective is the method usually employed of passing the material in its *damp* condition direct into the tartar emetic bath. The difference is specially noticeable in the soaped swatches.

As to the proper concentration of the tartar emetic bath to be employed, this cannot be authoritatively determined on the small scale, but, of course, the aim must always be to thoroughly fix, or render insoluble, the whole of the tannic acid present in the fibre. By a few experiments on the large scale it will be easy to find what amounts of tartar emetic must be used, in order to leave as little excess as possible in the fixing-bath. If the goods pass through the bath in a continuous manner, they are, of course, only immersed for a very short time, and the solution must then be made more concentrated, and continuously replenished from a stock solution, in order to ensure the presence of a slight excess of tartar emetic. Only by experiments made on the large scale in the dye-works is it possible to determine also what evil effects are produced by the passage of a large number of tannin-prepared pieces through the same tartar emetic bath.

The addition of such salts as ammonium chloride, &c., to the fixing-bath, for the purpose of facilitating precipitation, may also be tried.

One point still remains to be determined, namely, the proper temperature of the fixing-bath, and this may be ascertained by an additional series of experiments, similar to those instituted in the case of fixing Catechu by means of potassium dichromate.

Stannic chloride, zinc acetate, &c., also precipitate tannic acid from its solutions, and if on economical grounds it is desired to substitute these for tartar emetic, the most favourable conditions of concentration, temperature, &c., with respect to these, must be determined according to the above method. Finally, parallel experiments must be made with the best methods of employing the different fixing-agents, as previously determined, and the most convenient may then be selected.

429. Experiments with Colouring Matters.—Should the problem to be solved relate to the application of a coal-tar colour to wool or silk, one must determine whether the dyeing should take place in a neutral or acid bath. In the case of silk, one may try the utility of adding "boiled-off" liquor to the bath, and, having determined the best amount to use, one proceeds, in the event of an acid bath being required, to determine the proper kind and exact amount of acid to add. One may also try the use of acid salts—*e.g.*, alum, cream of tartar, &c.—instead of free acid. Here, too, experiments must be made to see whether it is better to dye in a cold or hot bath, or how high the temperature should be raised, and in what time the highest limit of temperature should be attained, &c.

In some cases, an alkaline dye-bath may be found the best—*e.g.*, with Alkali Blue—on wool and silk. Since both these fibres are more or less attacked by alkalis, especially under prolonged influence and at a high temperature, &c., it becomes imperative to make experiments for the purpose of choosing the least injurious form and the minimum amount of alkali, also the proper temperature, duration of boiling, &c.

In studying the application of such colouring matters as require the aid of mordants, the necessary experimental work becomes even more difficult than in the cases already cited. The following considerations, for example, require to be taken into account: 1, the particular kind and amount, or concentration, of mordant to employ; 2, the conditions of mordanting—duration, temperature, &c.; 3, the fixing of the mordant. As to the subsequent dyeing, the experiments partake of the character of those already mentioned.

As an illustration of the kind of experiments pursued in respect of mordants, the application of an aluminium salt to cotton and to wool will now be sketched.

430. Experiments in Mordanting Cotton.—Cotton is scarcely ever mordanted with aluminium sulphate, but rather with aluminium acetate, for reasons which have already been given in the chapter on Mordants. The compound $Al_2\,SO_4(C_2H_3O_2)_4$ will be here considered.

Several solutions containing this compound may be made, and of such concentration, for example, that they contain what is equivalent to 10, 20, 40, 60, 80, 100 grams of $Al_2(SO_4)_3{\cdot}18H_2O$ per litre.

Separate pieces of calico or cotton yarn are impregnated as evenly as possible with each of these solutions, and are then exposed for about two days to a moist warm atmosphere in an ageing chamber, in order to allow the acetic acid to evaporate. After such treatment there remains on the fibre a basic salt, of the composition $Al_2O_3{\cdot}SO_3$, which, neglecting the water of hydration, may also be represented thus: $Al_2O_3{\cdot}3SO_3 + 2Al_2O_3$. From this it becomes evident that for full and complete precipitation on the fibre, the latter should be passed through a weak alkaline bath, in order to remove the sulphuric acid still present.

For this purpose, one may compare the use of silicate, arsenate, phosphate, and carbonate of soda or ammonia, or simply chalk suspended in water, &c. Of these salts, it is advisable to employ solutions of various degrees of concentration, but containing *equivalent amounts* of substance. Such several solutions are used both cold and at a temperature of 50°—60° C. The mordanted cotton is well worked therein for 2—3 minutes, until thoroughly wetted, then washed well, and properly dyed, using a slight excess of colouring matter, *e.g.*, Alizarin.

It is advisable to dye for some time in the cold solution, then to raise the temperature slowly, *e.g.*, in the course of an hour, to 60° C. If the swatches seem not to take up any more colouring matter—*i.e.*, if the mordant is saturated—they are well rinsed in water, and one half of each is moderately well soaped. After drying, the various swatches are compared with each other as to colour, and with a little practice one is soon able to determine which fixing-bath gives, relatively, the best result. In using Alizarin, it is well to remember that the dye-bath must contain a certain percentage of calcium acetate.

431. Experiments in Mordanting Wool.—Since the method of mordanting wool differs from that employed for cotton, experiments on the application of mordants to this fibre assume another form. With regard to aluminium mordants, for example, the ordinary plan is to boil the wool with a solution of alum or aluminium sulphate, with the addition of cream of tartar, and one has to determine the relative and absolute amounts of these constituents to be employed, in order to give, for example, the best red with Alizarin.

For this purpose, six mordanting-baths are prepared, each containing, say, 1 litre of distilled water, and such amounts of $Al_2(SO_4)_3 \cdot 18H_2O$ as are equal to 2, 3, 4, 6, 8, 10 per cent. of the weight of wool employed. It is convenient to take 10 grams of wool for each vessel. The mordanting-baths are then simultaneously heated, so that their temperature may be raised to the boiling point, say in the course of one hour, and the wool is boiled for half an hour longer. The swatches are then well washed and dyed simultaneously in separate baths, with equal weights of Alizarin.

The dyeing is conducted in a manner similar to that given for cotton, but it is here necessary that towards the end of the operation the wool be boiled. The addition of calcium acetate to the dye-bath is also necessary. If excess of Alizarin has been used in the dye-bath, it should be removed by boiling the dyed swatches in distilled water.

After drying, the swatches are compared with each other, and the necessary amount of aluminium sulphate to employ is fixed upon, *e.g.*, 6—8 per cent. A second series of mordanting experiments should then be made, in which equal weights of wool are mordanted, say with 6 per cent. of aluminium sulphate alone, and also with the addition of increasing amounts of cream of tartar. It is convenient to consider the amount of aluminium sulphate employed as representing 1 molecule of the salt, and to add the cream of tartar to the several baths, in the proportion of 0, 1, 2, 3, 4, 6 molecules. The method of mordanting and dyeing is conducted exactly as already described, and on comparing the colours of the dyed swatches, it is easy to determine whether or not the addition of cream of tartar to the mordanting-bath has been at all beneficial, and, if so, which amount gives the best result.

Since, in the case of wool and silk, the mordant may be applied before, after, or simultaneously with the colouring matter, other series of experiments must be carried out in order to determine which of these methods is the best.

In comparing the dyed swatches, not only is the intensity, purity, brilliancy, regularity, &c., of the colour taken into account, but also the effect produced upon the fibre, and the behaviour of the colour towards washing, soaping, scouring, milling, rubbing, light, &c.

In all cases of experimental dyeing, indeed, it is essential to conduct the experiments under conditions as similar as possible to those which are met with on the large scale, and in judging of the results, great care must be taken to avoid the possibility of referring any effect produced to more than one cause at a time.

To sum up the whole system of experimenting on the application of colouring matters by dyeing, it may be said that, in order to determine the effect of each particular ingredient used, the dyer must perform simultaneously two or more distinct experiments, in which equal weights of the same textile material are submitted to all the necessary operations under precisely the same conditions, except as regards the amount employed of the ingredient whose action is to be studied.

Whatever, indeed, be the factor the influence of which is to be determined, whether it be the duration or temperature of mordanting or of dyeing, the character or amount of the several ingredients employed, and so on, *that factor alone* is varied, while the others remain unchanged. In this way a systematic series of dyeing experiments is carried out; one by one the nature and value of each individual influence is carefully ascertained, until at length, by a cumulative process, the *totality of conditions* necessary to produce the best results is accurately determined. The actual number of experiments which it may be requisite to perform with any given colouring matter, before arriving at a full knowledge of its dyeing properties, is quite indefinite, and is more or less influenced by the character of the colouring matter, and by the general and special chemical knowledge of the experimenter.

Far too frequently, it is to be feared, the dyer neglects or declines to institute dyeing experiments on the above lines, but regards them either as of little use, or as too costly, or as taking up too much time, ignoring or forgetting that the knowledge thus obtained invariably leads to almost absolute certainty in carrying out dyeing operations on the large scale, and repays a thousandfold the time and trouble expended.

As to the apparatus required, it is comparatively simple. A water- or steam-bath, or an oil- or glycerine-bath, heated with gas or steam, provided with a perforated cover for the reception of the dye-vessels, serves for the simultaneous and equable heating of the latter. The dye-vessels themselves should be of toughened glass or well-glazed porcelain, and capable of holding about half a litre or even one litre. Metallic vessels of whatever kind, although very useful for special work, are not to be recommended for general use, especially for experimental *wool*-dyeing, since the acids and acid salts so frequently used in mordanting and dyeing invariably dissolve traces of the metal, which, in many cases, affect the ultimate result.

For the same reason, stirring-rods or other apparatus for moving the textile material during the mordanting or dyeing process, must also be of glass or porcelain. A good balance, a few glass beakers, porcelain basins, measure glasses, burettes, pipettes, and hydrometers, complete the equipment.

Figs. 96 and 97 show plan, elevation, and section of a very convenient arrangement for experimental dyeing (made by Messrs. Broadbent and Sons, Huddersfield). It consists of a couple of strong cast-iron pipes B, into which iron cups C, for holding glycerine, are screwed. The porcelain dye-vessels A rest in the glycerine cups, and are clamped down by means of a flange,

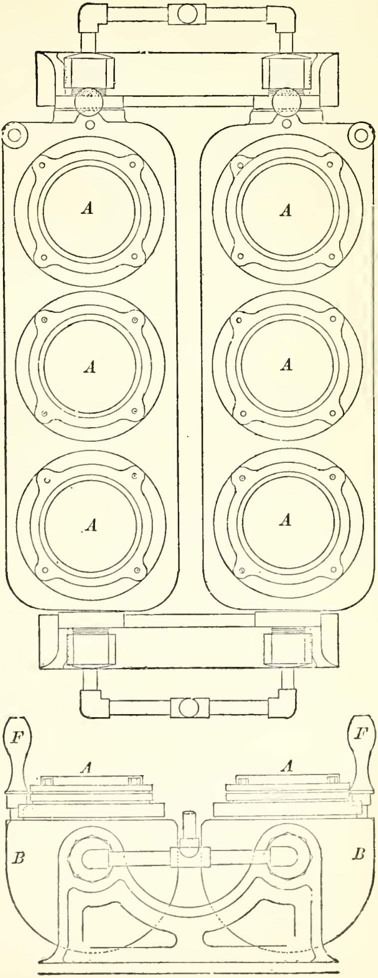


Fig. 96.—Plan and Elevation of Experimental Dyeing Apparatus.

protected with india-rubber or asbestos rings. The pipes B are so supported that they can be readily turned on their axes, by means of the handles F, for the purpose of emptying the dye-vessels. The axes are hollow, and serve respectively for the introduction of steam at D, and the escape of condensed water at E. One of the difficulties hitherto encountered in experimental dyeing arrangements is that of being able to heat the water in a series of *porcelain* dye-vessels to the boiling point simultaneously, and in a sufficiently convenient and cleanly apparatus. The one here shown, in which steam at 50—60 pounds' pressure is used, will be found to answer every requirement.

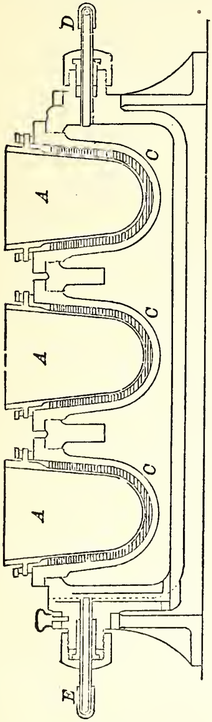


Fig. 97.—Section of Fig. 96.

432. Exposure of Dyed Patterns to External Influences.—Although in the above, reference has been made to the method of determining the conditions of dyeing, &c., necessary to obtain the brightest, most intense, and best colours, it must not be forgotten that a dyer knows but half his business if he is simply acquainted with these conditions. He must not only learn how best to apply any given colour; he must also know the capabilities of each dyed colour: how it withstands the action of light, milling, scouring, &c.,—in short, all those influences, whether natural or artificial, to which the dyed fabric is likely to be submitted. Hence, all dyers should habitually and systematically expose portions of dyed patterns to the several influences just mentioned, and, as already stated, all care must be taken to avoid the possibility of referring any effect produced to more than one cause at a time. Such exposed patterns must be afterwards carefully compared with the original patterns as dyed.

433. Fastness of Colours.—The term "fast colour" generally implies that the colour in question resists the fading action of light, but it may also imply that it is affected by washing with soap and water, or by the action of acids and alkalis, scouring, milling, rubbing, bleaching, &c. In its wide sense, it means that the colour is not affected by any of those influences to which it is destined to be submitted, but its technical meaning is often restricted. To the cotton-dyer, for example, it may refer chiefly to washing with soap and water, and to light. To the woollen-dyer it may refer to milling, scouring, and light; and so on.

Many colours may be fairly fast to washing with soap and water, and yet be very fugitive towards light; or they may be fast to light, and yet very sensitive to the action of acids or alkalis.

The term "loose colour" generally implies that the colour is much impoverished, or even entirely removed, by washing with water or a solution of soap; it may, however, also mean that it is not fast to light.

The word "permanent," as applied to colour, generally denotes that it is fast to light and other natural influences.

A "fugitive colour" is generally understood to be one which is not fast to light, or which volatilises more or less under the influence of heat.

In the absence, then, of any definite meaning being attached to the above terms, it becomes imperative, in speaking of the fastness of a colour, to refer specially to the particular influences which it does or does not resist.

434. Influence of Light on Dyed Colours.—The chemical activity of the sun's rays is well known, and it has already been noticed that certain unstable mordant solutions seem to be decomposed and precipitated more readily under the influence of light. It is not surprising, therefore, to find that light should also have a very marked effect upon dyed colours. Under the prolonged influence of light and air almost all colours fade, and according to their relative behaviour in this respect, they are broadly divided into two classes, namely, those which are "fast to light," and those which are "not fast to light." There is, however, no definite line of demarcation between the two, and dyed colours are met with possessing all possible degrees of resistance.

Each of the coloured rays of the spectrum possesses a different fading power. White light is the most active, then follow the yellow, blue, green, orange, violet, and red rays. Direct sunlight is more energetic than diffused daylight. The light of the electric arc acts in the same sense as sunlight, but is less powerful (about one fourth).

According to Chevreul, the presence of oxygen and moisture assists very materially in the fading action of light, so that even some fugitive colours, dyed, for example, with Safflower, Annatto, Orchil, do not fade if exposed to light in dry oxygen or *in vacuo*. Chevreul has shown, too, that the nature of the fibre has considerable influence in the matter, and that some colours are less fugitive on cotton than if fixed on wool or silk. Whether the essential action of light is one of oxidation or of reduction, or whether the action varies with each colouring matter, has not yet been determined. In the case of Prussian Blue, it is said to be one of reduction, but from the fact that air and moisture play generally an important part in the fading process, it is quite conceivable that in many cases it is one of oxidation. It is known that during the evaporation of water, ozone or hydrogen peroxide is found in small quantities, and both are powerful oxidising, as well as bleaching, agents.

Heat is found to act in some cases in the same sense as light, but in a very inferior degree.

The following notes referring to the fastness of colours are taken from experiments made with dyed wool, samples of which were exposed to the light during periods of one, two, four, eight, and twelve months.

The division of the colouring matters into "fast," "medium," and "fugitive," is more or less approximate, and is merely intended to convey in a simple manner the general character of each.

Red Colours.

Fast. Alizarin (Al), Isopurpurin, Purpurin, Flavopurpurin, Nitro-alizarin (Cu), Madder.

Medium. Cochineal (Sn, Al), Biebrich Scarlet and allied colours.

Fugitive. Many of the Azo Reds and Scarlets, Magenta, Safranine, Aurin, Eosin, and allied colours; Peachwood (Al, Sn), and allied red woods; Barwood (Al, Sn), Sanderswood (Al, Sn), Ammoniacal Cochineal (Sn).

Orange and Yellow Colours.

Fast. Iron Buff, Chromate of lead yellow, Canarin, Chrysamin on cotton (F. Baeyer), Orange G (M. L. & B.), Nitro-alizarin (Sn, Al), Alizarin (Sn), Isopurpurin (Sn), Flavopurpurin (Sn).

Medium. Croceïn Orange, Diphenylamin Orange, β Naphthol Orange, Azoflavin, Brilliant Yellow, Fast Yellow, other coal-tar yellows, Weld (Sn), Old Fustic (Sn), Quercitron Bark (Sn), Flavin (Sn), Persian Berries (Sn).

Fugitive. α Naphthol Orange, Chrysoïdine, Phosphine, Fluoresceïn, Turmeric, Annatto, Young Fustic (Sn).

Green and Olive Colours.

Fast. Cœruleïn, Naphthol Green, Persian Berries (Cu).

Medium. Weld (Cu, Fe), Old Fustic (Cu, Fe), Quercitron Bark (Cu, Fe), Flavin (Cu, Fe).

Blue Colours.

Fast. Vat Indigo, Alizarin Blue, Prussian Blue.

Medium. Logwood (Cu, Fe, Cr), Indulines.

Fugitive. Alkali Blues, Soluble Blues, Spirit Blues, Indigo Carmine, Methylene Blue (this is very much faster on cotton), Logwood (Al).

Purple Colours.

Fast. Alizarin (Fe, Cr), Isopurpurin (Fe), Galleïn (Cr, Cu).

Medium. Galleïn (Al, Fe), Cochineal (Cr, Fe), Gallocyanin.

Fugitive. Logwood (Sn), Ammoniacal Cochineal (Al), Orchil, Limawood (Cr, Fe), Methyl Violet, Hofmann's Violet, Perkin's Violet, Rosaniline Violet.

Brown Colours.

Fast. Nitro-alizarin (Cr), Isopurpurin (Cr, Cu), Flavopurpurin (Cr, Fe. Cu), Purpurin (Cr, Fe, Cu), Madder (Cr, Fe, Cu), Cochineal (Cu), Catechu.

Medium. Camwood (Cu, sadden).

Fugitive. Camwood (Cr, Cu, Al, mordant and dye), Barwood (Cr, Cu), Sanderswood (Cr, Cu), Bismarck Brown, other Azo Browns.

Some colouring matters — *e.g.*, Alizarin — give fast colours with all mordants; others—*e.g.*, Limawood and Young Fustic—seem only capable of yielding fugitive colours; others again—*e.g.*, Logwood—give fast or fugitive colours, according to the mordant employed. The fugitive character of the colours obtained from Logwood by the use of tin and aluminium mordants, compared with the medium fastness of those obtained when copper, chromium, or iron mordants are employed, is rather striking.

Some colours present somewhat abnormal properties. Wool mordanted with aluminium and tin mordants, and dyed with Camwood, yields reddish-brown colours, which during exposure become at first considerably darker, and begin to fade only after two or four months. The olive-green colour yielded by Persian Berries and copper sulphate is quite remarkable in this respect, since it actually becomes darker and greener, even after an exposure of twelve months. The pure greenish-yellow obtained with Picric acid exhibits a similar character; on exposure it rapidly becomes orange, and this begins to fade only after a lapse of about twelve months.

The mode of application also influences the fastness of the colour. Camwood and Catechu, for example, yield faster colours with copper sulphate by the saddening method than by the mordanting and dyeing method.

In studying the behaviour of the coal-tar colours towards light, one cannot fail to be struck with the manifest influence of their chemical constitution in the matter. All those colouring matters, for example, in which the atomic arrangement is like that of Magenta, are similarly fugitive to light, *e.g.*, Methyl Violet, Benzaldehyde Green, &c.; such similarity extends even to Aurin and Safranine. Colouring matters allied to Alizarin, on the other hand, all possess the quality of fastness to light. There are, however, cases in which an apparently slight difference in constitution gives rise to remarkable differences in fastness to light—compare, for example, Fluorescein and Galleïn, Indigo Carmine and Vat Indigo Blue.

The popular fallacy that coal-tar colours are fugitive, and that the colours yielded by dyewoods are fast, has already been shown to be false, and is only referred to because it still lingers in the minds of some dyers. The origin of a colouring matter has of course nothing whatever to do with its properties: these are mainly, if not entirely, governed by its chemical composition and constitution.

435. The Dyeing of Compound Shades.—Comparatively few of the colours met with on dyed fabrics result from the employment of a single colouring matter; it becomes imperative, therefore, for the dyer to know how to apply two or more together. This knowledge can readily be gained by making a series of dyeing experiments

The result obtained by mixing, as it were, the dyed colours must be observed and studied much in the same way as the artist does with the pigments upon his palette.

None of the colours here dealt with are pure, like those of the physicist; hence the product of the mixture of dyed colours is for the most part totally different to what would be produced by combining together the various colours of the spectrum.

A mixture of red and yellow produces *orange*, yellow and blue produce *green*, blue and red produce *violet*, green and violet produce *blue*. Orange and Green tend to produce *yellow ;* violet and orange tend to produce *red.*

The compound colours, orange, green, and violet, vary in shade according to the amount and purity of tone of each constituent single colour. If, for example, in combining yellow and blue, the yellow inclines to orange, or the blue inclines to purple, the green produced inclines to olive.

With the physicist, white is produced either by a mixture of all the colours of the spectrum, or by mixing together what are known as "complementary colours," for example the following :—

Purple and green.
Red and bluish-green.
Orange and turquoise blue.
Yellow and ultramarine blue.
Yellowish-green and violet.

With the dyer, however, the opposite effect tends to be produced. A judicious mixture of red, yellow, and blue tends to produce sombre colours or even black. In the same way red and green produce chocolate or brown, blue and orange produce drab, &c.

It is beyond the scope of this manual to discuss the law of the mixture of colours. For information on this point the reader is referred to Bezold's "Theory of Colour," Rood's "Modern Chromatics," and other similar works. It is, however, always imperative, in the end, to gain positive and reliable information by actually making special dyeing experiments, and even then, long experience is required before one feels thoroughly at home in producing any given compound shade.

A very necessary, or at least desirable, point to remember is, that all the colouring matters employed simultaneously should be really applicable to the best advantage, by the same process. A colouring matter which requires to be applied in an acid-bath ought not to be applied simultaneously with one which dyes best in a neutral bath. Basic colouring matters, although not requiring mordants, can, however, be frequently employed along with such as do, whenever the "mordanting and dyeing method" is used, since the latter are almost invariably applied in a neutral dye-bath.

If the compound shade is intended to be fast towards any influence—*e.g.*, light, milling, &c.—then each constituent colour yielded by the several dyestuffs, when separately employed, should be as similar in fastness to that influence as possible.

Although dyers frequently apply fast and fugitive colours together in producing compound shades, or for the sake of improving the brilliancy of any given colour, it is always more or less irrational, and ought to be avoided whenever possible.

436. Influence of Milling.—The process of "milling," so much used in the heavy woollen trade for Tweeds, &c., consists in saturating the woollen cloth with a strong solution of soap (frequently carbonate of soda as well), and then submitting it to a violent kneading, beating, or pressing, in the wash-stocks (*see* Fig. 52) or "milling machine." It is an exceptionally severe treatment, and demands of the colour: that it shall withstand rubbing, that it shall not be decomposed by or be soluble in weak alkalis, and that whatever colour does rub off, this shall not permanently stain contiguous fibres (bleeding). As a general rule the best colouring matters in respect of the last point are those which require the aid of mordants, *e.g.*, Alizarin, Logwood, &c. Coal-tar colours, which are applied directly, *e.g.*, Magenta, Azo Scarlets, &c., are very prone to dissolve off and dye the neighbouring fibres.

Some acid-colours are unsuitable because they are more or less decolorised by the action of the alkali, *e.g.*, Acid Magenta, Acid Green, Alkali Blue, Alkali Green, &c. In such cases the original colour can be more or less restored by a passage through dilute acid, preferably acetic acid.

CHAPTER XXV.

ESTIMATION OF THE VALUE OF COLOURING MATTERS.

437. In order that the dyer may produce good and regular work, it is essential that the conditions under which he labours be maintained as regular as possible. The mordants and colouring matters he employs should be of good quality, free from injurious admixture, and of constant composition.

The certainty of obtaining such requisites can only be relied upon by exercising constant care and supervision in their selection, which should always be based on the results of analysis or practical experiment.

The purity and value of mordants can, as a rule, be determined by the ordinary methods of chemical analysis; not so, however, with colouring matters, since their analytical behaviour has been for the most part neglected.

438. **Colorimetry.**—The rapid determination of the comparative colouring power of any given colouring matter, by means of the colorimeter, has only partially and inadequately solved the problem, and it has in most cases little practical value.

The instrument consists of two calibrated tubes of equal diameter and length, into which are put the solutions of equal weights of the two colouring matters to be compared with each other. As a rule, one solution appears darker than the other, and this must be diluted with some of the solvent until both solutions are equal in intensity of colour. The colouring powers of the two dyestuffs are proportionate to the volumes of the diluted solutions.

One difficulty which presents itself is, that a fair comparison can only be made when the colouring matters under examination are free from coloured impurities, and are exactly of the same tint.

439. **Comparative Dye-Trials.**—The most practical and satisfactory method of estimating the relative value of colouring matter is to make a series of comparative dyeing experiments on a small scale.

In these experiments the fibre dyed should be the same as that to which eventually the colouring matter is to be applied, and, as far as possible, exactly the same process of dyeing, and all necessary subsequent operations should be adopted as are employed on the large scale.

When it is desired to choose the best sample from a number of colouring matters which are offered for sale, equal weights of cotton-, wool-, or silk-yarn, are dyed with *equivalent values* of the several samples, in which case that sample which gives the best results is of course the cheapest, whatever its actual price may be.

It is advisable that comparative dye-trials of this kind should be made with all the colouring matters in general use, and samples of the best and cheapest (*i.e.*, those adopted) should be carefully preserved in stoppered bottles, to serve as "standards," or "types."

Aged or moist dyewoods (*e.g.*, Logwood) should be previously dried, to prevent deterioration. It afterwards becomes necessary to test in a similar manner all subsequent deliveries of each colouring matter, and to compare them with their respective "standards."

One essential condition of success in making comparative dye-trials is that the several portions of yarn or cloth should be dyed simultaneously, and under exactly the same conditions as to time, temperature, &c. The most convenient dye-bath arrangement is that consisting of six or eight glazed porcelain or hardened glass dye-vessels, each of 250°—1000° cubic centimetres capacity, immersed in a common water-, oil-, or glycerine-bath, suitably heated by gas or steam, or the arrangement illustrated on pp. 483, 484.

Ground dyewoods, after weighing, may be at once put into the dye-vessels, but it is best, first to prepare solutions of extracts, pastes, or soluble colouring matters, particularly if of high colouring power (*e.g.*, coal-tar colours). For example, 0·1—1 gram is dissolved in 100 cubic centimetres of water or alcohol, and the requisite quantity of solution is introduced into the dye-vessel by means of a pipette.

Swatches of cloth are distinguished from each other by cutting small holes near the edges; yarn is marked by means of knotted threads. After filling the dye-vessels with cold water first, the colouring matter is introduced, then the cloth or yarn, previously wetted with water. It is well, as a rule, to dye for some time in the cold, in order to ensure perfectly even dyeing; and then, with constant stirring, to raise the temperature gradually, or exactly as one would do on the large scale.

After dyeing, the swatches are washed and dried; or if necessary a portion of each may be worked for half an hour or so in a hot soap solution, or otherwise cleansed and brightened, and then washed and dried.

The patterns are finally compared with each other under exactly similar conditions of illumination. Blue, violet, and green colours are frequently more accurately judged of by gaslight.

For those engaged in cotton-dyeing, it is convenient to employ in the above trials, calico printed with various mordants, in the form of broad stripes—*e.g.*, with iron and aluminium mordant separately—each in two degrees of concentration, and also with a mixture of the two. Such mordanted calico was originally in general use for testing the commercial value of Madder, but it can be very conveniently used in testing all those dyestuffs which are used in practice, in conjunction with the above mordants, for the production of serviceable colours: *e.g.*, the various dyewoods or their extracts, Alizarin, Galleïn, &c.

For those colouring matters which can be fixed by means of tannic acid, it is convenient to use calico padded or printed in stripes with tannic acid, and afterwards fixed in a tartar emetic bath, washed and dried.

For the woollen- and silk- dyer, it is best to dye equal weights of these materials, either in form of yarn or cloth. Whenever necessary they are first mordanted, and all the ingredients which it is necessary to employ on the large scale are added to the dye-bath.

The most difficult colouring matters to estimate are those which cannot be exhausted in the dye-bath; with such, dyers often dip white blotting-paper or calico, as equally as possible, into the solutions. It is allowed to drain, and then dry, and a comparison of the colours on the stained paper is made.

In certain cases, fractional dyeing gives information as to foreign matter or impurities present in a colouring matter. A concentrated dye-bath is prepared, 0·1 metre of cloth is dyed in it, and after its removal a second, third, fourth, &c., are dyed in the remaining solution, until the bath is exhausted. If the colouring matter is pure, the different swatches should not vary in tone, although they may do so in intensity.

The purification of certain colouring matters by the manufacturer entails considerable loss. The cheaper qualities of Rosaniline Blue always contain reddish-violet colouring matter; hence, a pure blue (*e.g.*, 6 B) gives a weaker colour than the cheaper reddish-blues. For certain purposes, the latter are indeed preferable to the former, *e.g.*, for the production of compound shades.

The dyer is strongly recommended not to be deterred from making exact dyeing trials because of the (comparatively little) trouble they give, for he will only in this manner properly estimate the worth of his dyestuffs, and avoid irregular or bad work.

It is probable that if the testing of dyestuffs before using them, were only generally adopted, the custom would cease of mixing or diluting colouring matters with useless bodies—*e.g.*, dextrin, sugar, sand, &c.—which has been forced upon the colour manufacturer, because of want of judgment, on the part of many dyers, who wish only to buy *cheap*.

In order to recognise the individual colouring matters, one makes all possible use of the reactions dependent upon their chemical properties.

Mixtures of colouring matters are recognised sometimes by the following methods : a strip of white blotting-paper is partly immersed in the solution, when it frequently happens that the different colouring matters exhibit different degrees of capillary adhesion, and different zones of colour are perceptible on the paper ; or a little of the finely-powdered colouring matter is dusted over white blotting-paper, moistened with water or other suitable solvent, or it is dusted over a glass vessel containing the solvent in a perfectly still condition. If the colouring matter is a mixture, differently-coloured spots appear on the paper, or streaks of the different colour solutions are seen in the solvent. Such an appearance is well shown by coal-tar colour mixtures, intended to give indigo-blue shades : they give violet, orange, and green spots or streaks. It is also conceivable that the different constituents of a colour mixture are not all soluble in the same solvent—a fact which may also serve to differentiate them.

Chemical methods of estimating the value of colouring matters cannot always be accepted as wholly reliable. As a rule, standard solutions of oxidising agents are employed—*e.g.*, bleaching-powder, potassium chlorate or dichromate in acid solution, or potassium ferrocyanide in alkaline solution—and these are added until the colour is destroyed.

These and other methods will be found in works on chemical analysis.

CHAPTER XXVI.

THE DETECTION OF COLOURS ON DYED FABRICS.

The mode of determining what colouring matters are present on dyed fabrics, leaves much to be desired. The analytical behaviour of colouring matters has been somewhat neglected, and reactions which can be carried out with ease and certainty by means of a few simple tests are rare. With compound shades the difficulty is increased, and the behaviour of a colouring matter towards reagents often varies considerably according to the fibre and the mode of application.

In many cases the analysis of the mordant accompanying the colouring matter gives definite information as to the nature of the latter, hence its examination should not be neglected. Inorganic mordants are recognised by calcining a portion of the dyed material and examining the remaining ash according to the usual analytical methods. Sometimes it is desirable before calcining to destroy the colouring matter present, *e.g.* by boiling with a dilute solution of bleaching powder, that is if there is no fear of destroying the mordant thereby. The detection of organic mordants occurring along with inorganic ones, is difficult, and each case must be specially treated.

In examining dyed fabrics for colour, according to the following tables, small portions are cut off and steeped in porcelain basins containing a little of the several reagents named, moderately concentrated. Other portions should also be heated in test-tubes with dilute solutions.

Having thus determined what colouring matter is present, parallel tests should be applied to fresh material of the same fibre as that under examination, specially dyed with the suspected colouring matter. In this manner the conclusions are confirmed or otherwise, and a certain degree of accuracy is introduced.

RED

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Magenta.	Fibre and solution yellow, colour restored on washing.	As with HCl.	Fibre at first paler, afterwards nearly colourless, especially on heating.	Fibre decolorised.
Acid Magenta. (BASF)	Faint bluish-red liquid extracted, colour of fibre unchanged.	As with HCl.	Fibre decolorised in the cold.	Fibre decolorised, colour gradually restored on exposure to air.
Safranine. (B. S. & S.)	Dilute, no action; concentrated, fibre blue.	Fibre at first black, which soon changes to green.	Solution pink.	As with NaOH.
Eosin, A. (BASF)	Fibre pale yellow.	Fibre at once bright yellow.	Fibre yellow, liquid pink fluorescent.	Fibre yellow, liquid yellow fluorescent.
Methyl-eosin.	Fibre yellow.	Fibre yellow.	Fibre pink, liquid pink fluorescent.	As with NaOH.
Erythrosin, I. (BASF)	Fibre brownish-yellow.	Fibre yellow.	Fibre and liquid pink.	As with NaOH.
Phloxin, J. (P. Monnet & Co.)	Fibre yellow.	Fibre yellow.	Fibre and liquid pink.	Fibre and liquid pink.

COLOURS.

$SnCl_2$ + HCl.	Alcohol.	Other Tests.
Almost entirely decolorised on boiling; colour partly restored on washing.	A bluish-red liquid readily extracted.	Sodium sulphide decolorises. Magenta may be distinguished from Orchil and Aurin as follows: Amyl Alcohol extracts a bluish-red colour from material dyed with Magenta. Amyl Alcohol extracts a yellow colour from material dyed with Aurin. Amyl Alcohol extracts a pink or violet colour from material dyed with Orchil. To the Alcoholic extract add NH_4OH, Magenta is decolorised. To the Alcoholic extract add NH_4OH, Aurin turns bluish-red. To the Alcoholic extract add NH_4OH, Orchil remains unchanged.
Colour largely extracted on boiling.	Very little colour extracted.	
Decolorised on heating, liquid colourless.	Colour extracted, red fluorescent solution.	
Fibre orange-yellow, solution pale yellow.	*Soluble* Eosines not extracted if well dyed. *Spirit* Eosines readily extracted by absolute alcohol.	Hot water containing a little NH_4OH extracts a pink liquid from soluble Eosines. Boiled with concentrated KHO (20—40 per cent.), Eosin G gives orange-red solution, which on continued boiling becomes purple, and finally blue with strong green fluorescence. Colour and fluorescence unchanged on dilution. Eosin B boiled with KHO gives bluish-violet solution with pale green fluorescence. On dilution, liquid becomes reddish-purple.
... ...	Pink fluorescent solution.	Eosin BN boiled with KHO gives eventually olive-green solution without fluorescence.
Fibre orange on boiling.	... ...	
Fibre yellowish on boiling.	... ...	

RED COLOURS

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Aurin.	Fibre yellow.	As with HCl.	Solution bright red.	As with NaOH.
Magdala Red.	No change.	No change.	No change.	No change.
Purpurin.	Boiled with dilute HCl, fibre orange yellow and liquid yellow.	As with HCl.	Heated with dilute NaOH, fibre and liquid cherry-red.	Boiled with dilute NH_4OH liquid pale pink, fibre not changed.
Alizarin.	Dilute, no action; concentrated, fibre bright yellow, liquid amber yellow.	Dilute, no action; concentrated, red colour extracted. Concentrated H_2SO_4 at the ordinary temperature entirely dissolves cotton dyed with aliz. red, and the alizarin separates out as a flocculent precip. which may be collected, dried and sublimated. Or, if not, it may be recognised by the violet coloration imparted by alkalis.	Fibre and solution violet.	No action.

(continued).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
In the cold solution yellow.	Colour extracted.	
Little action, fibre slightly blue.	Very slightly extracted. Solution fluorescent pink.	To detect Magdala Red on silk dyed with a mixture of Magdala Red and Eosin, extract with boiling alcohol, which dissolves out the Eosin, and test the solution in the ordinary way. Wash the silk and test for Magdala Red with acids and alkalis.
Fibre brownish-red, liquid amber-yellow.	Solution red.	HNO_3 gives a bright yellow spot. Bleaching powder bleaches it. $Ba(OH)_2$ turns fibre cherry-red and extracts a pale bluish-red solution. Boiling with a solution of aluminium sulphate and cooling, gives an orange fluorescent solution.
Fibre orange-yellow, liquid bright yellow.	No action.	Gives no fluorescent solution on boiling with $Al_2(SO_4)_3$ (distinction from Madder and Purpurin). Bleaching powder and chromic acid bleach it. Boiled with $Ba(OH)_2$ solution, fibre becomes violet, HNO_3 gives a yellow spot. An alkaline solution of K_3 $FeCy_6$ has no action, nor has $KMnO_4$. HNO_2 vapour converts it into yellow Nitro-alizarin. On heating, Alizarin red loses brilliancy and becomes brownish, but regains most of the brilliancy on exposure to air. The ammoniacal, aqueous, or alcoholic solutions give characteristic absorption spectra.

RED COLOURS

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Croceïn scarlet 7B. (F. Baeyer & Co.)	Fibre at first violet, liquid colourless. On standing, fibre becomes blue, liquid greenish-blue.	Concentrated acid, fibre and solution blue.	Colour of fibre blue.	
Biebrich Scarlet. (Kalle & Co.)	Fibre violet, liquid colourless. On standing, liquid becomes greenish-blue.	Fibre and solution green.	Fibre dark bluish-red, liquid colourless.	No action.
Patent Fast Red. (BASF)	Fibre darkened, liquid slightly tinged red.	Fibre violet, liquid colourless, but on standing bluish-violet.	Fibre made paler, and red colour extracted.	No action.
Fast Ponceau B. (BASF)	Fibre violet, liquid colourless. On standing, liquid becomes greenish-blue.	Fibre and solution green.	Fibre dark bluish red, no colour extracted.	No action.
Scarlet 2 R. (M. L. & B.)	Fibre not changed by cold HCl, but on boiling nearly decolorised and much colour extracted.	Dilute H_2SO_4, no action. Concentrated H_2SO_4 extracts the colour.	Nearly decolorised.	Fibre paler.
Scarlet 3 R. (M. L. & B.)	Fibre not changed even on boiling. Bluish-red liquid extracted.	No action.	Nearly decolorised.	Little effect.

(*continued*).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre decolorised.	Little or no action.	HNO_3 gives at first a dark blue spot which changes to bright yellow with a greenish-blue border
Fibre decolorised.	Little or no action.	HNO_3 gives at first a dark blue spot which changes to brown with a dark blue border.
Fibre decolorised. (Resists this test better than other scarlets.)	Little or no action.	HNO_3 acts as with Croceïn Scarlet 7 B.
Fibre decolorised.	Little or no action.	HNO_3 gives a dark blue spot which changes to red brown with a dark blue or black border.
Fibre decolorised.	Little or no action.	HNO_3 gives violet spot which afterwards changes to bright yellow.
Fibre decolorised.	Little or no action.	HNO_3, as with Scarlet 2R.

RED COLOURS

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Claret Red B. (M. L. & B.)	Fibre little changed, liquid reddish violet.	Fibre at first violet, finally blue. Liquid at first colourless, afterwards bright blue.	Fibre orange-red, solution yellowish-red.	No action.
Madder. . .	Fibre brownish-red.	Fibre brownish-red, solution red.	Fibre and solution purple.	Wool brownish-red, cotton not changed.
Cochineal. .	Fibre orange-red, solution orange-pink.	Fibre and solution bright pink.	Solution purple.	As with NaOH.
Peachwood. .	Fibre dark red, solution pink.	Fibre brown, solution yellow changing to brown.	Much colour extracted, bluish-red. Cotton almost decolorised.	As with NaOH.
Barwood. .	No action.	Fibre reddish-brown, solution dirty brown.	Fibre purplish, solution colourless.	As with NaOH.
Sanderswood.	No action.	Fibre and solution reddish-brown.	Fibre purplish, solution colourless.	As with NaOH.
Safflower. .	Cotton decolorised.	Cotton decolorised.	With dilute NaOH, cotton pale yellow.	Cotton, flesh-colour.
Orchil. . .	Solution red.	Fibre and solution purple, afterwards brown.	Fibre bluish-purple.	As with NaOH.

(continued).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
On heating, fibre becomes almost colourless, or pale lilac.	Little or no action.	HNO_3 gives a violet spot which afterwards becomes brownish with a faint blue border. It is not affected so readily by HNO_3 as the Croceïn Scarlets are.
Little colour extracted.	No action.	Nitric acid colours fibre bright yellow.
Fibre and solution orange-red.	No action.	Nitric acid colours fibre yellow.
Fibre and solution bluish-red on heating.	Pale yellow solution.	Nitric acid colours fibre brownish-yellow. Boiling soap solution removes much colour, solution bluish-red.
Fibre unchanged, solution red.	Red solution.	Nitric acid colours wool dark olive.
Fibre unchanged, solution red.	Red solution.	Nitric acid colours wool dark olive. Boiled with $FeSO_4$ colour becomes violet.
Cotton straw yellow.	No action.	
At once decolorised.	Bluish-red solution.	See Magenta.

YELLOW AND

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Picric Acid.	Colour extracted on boiling, liquid greenish-yellow.	Decolorised.	Fibre becomes orange, solution yellow.	Fibre becomes paler, a yellow colour extracted on boiling.
Victoria Yellow.	Decolorised, washing restores the colour.	... ...	... ...	... ...
Naphthol Yellow.	Decolorised almost completely.	As with HCl.	Fibre orange, solution yellow.	Fibre paler, yellow colour extracted on boiling.
Naphthol Yellow S.	Fibre bleached, solution colourless.	Decolorised.	Fibre paler, liquid yellow.	Fibre little changed, liquid pale yellow.
Aurantia.	Fibre pale yellow.	Fibre yellowish-drab.	Little or no effect.	No action.
Chrysoïdine. (B. S. & S)	Fibre red.	Yellow colour extracted.	Fibre paler and yellower.	Fibre yellower.
Fast Yellow. (BASF)	Red	Fibre brownish-red, liquid red.	Solution brownish-yellow.	Little action.
Orange 3. (F. Baeyer & Co.)	Fibre red, liquid pink.	Fibre and liquid bright bluish-red.	Fibre dull yellowish red.	Fibre not changed, liquid slightly yellow.

ORANGE COLOURS.

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre bleached, the liquid colourless.	Yellow colour extracted.	All Picric Acid yellows taste bitter. Heated with KCN solution fibre becomes red through the formation of isopurpuric acid. In compound colours the cloth should be extracted with alcohol, and the solution tested for Picric Acid with KCN.
... ...	... ...	Warm water extracts the colour.
Fibre bleached, the liquid colourless.	Yellow colour extracted.	Water extracts the colour and the yellow solution is decolorised by H_2SO_4. Boiling KCN extracts a red colour. Wrapped in white paper and heated to 120° C., leaves a stain on paper.
Bleached.	No action.	Boiling water extracts nothing. Heated to 120° C. in white paper, leaves no stain.
Fibre brown on heating.	Colour readily extracted.	Heated with $SnCl_2$ gives dark brownish-red colour, afterwards decolorised.
Almost decolorised.	Yellow colour extracted.	
Fibre bright red, afterwards decolorised.	A little colour extracted.	HNO_3 gives a bright red spot.
Completely bleached.	A little colour extracted.	

YELLOW AND ORANGE

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Orange 4. (A. Poirrier)	Fibre reddish-violet, liquid violet.	As with HCl.	No action.	Fibre not changed, liquid yellow.
Orange 2. (A. Poirrier)	Fibre and liquid bluish-red.	As with HCl., but bluer.	Fibre deep red.	No action.
Phosphine.	Fibre nearly decolorised, solution yellow.	Solution greenish-yellow.	Fibre becomes paler and yellower.	Fibre becomes paler, a bright yellow.
Nitro-alizarin.	Fibre pale straw yellow, solution yellow.	Fibre brownish-yellow, liquid yellow.	Fibre claret-red or brownish, liquid colourless.	Cold, no action; hot, as with NaOH, but fibre not so dark.
Madder.	Little action.	Fibre brownish-red, solution red.	Fibre and solution purple.	Fibre brown.
Old Fustic.	Fibre and solution orange.	Fibre and solution brown.	Fibre little changed.	Fibre unchanged, solution yellow.
Young Fustic.	Fibre unchanged, solution pale yellow.	Fibre and solution reddish-brown.	Fibre reddish-brown.	As with NaOH.
Weld.	Fibre little affected, solution pale yellow.	Fibre brownish-yellow.	Fibre little affected, solution pale yellow.	No action.

COLOURS (*continued*).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
At first fibre becomes deep violet on heating, gradually lighter and finally bleached	Yellow colour extracted.	
Completely bleached.	No action.	
Fibre nearly decolorised.	A little colour extracted.	
Fibre deep yellow, liquid yellow.	No action.	HNO_3 gives a bright yellow spot. Boiling $Ba(OH)_2$ colours the fibre claret-red.
Fibre unchanged, solution pale red.	No action.	Heated with Fe_2Cl_6 fibre becomes olive-brown.
Fibre orange, solution colourless.	No action.	With HNO_3 fibre pale yellow. Heated with Fe_2Cl_6 fibre becomes olive. Boiled with acetate of alumina gives yellow solution with bluish-green fluorescence.
No action.	No action.	With HNO_3 fibre dark brown. Heated with Fe_2Cl_6 fibre becomes olive.
Fibre little affected.	No action.	HNO_3 no action. Heated with Fe_2Cl_6 fibre becomes olive. Colour unchanged by boiling with lead acetate.

YELLOW AND ORANGE

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Quercitron Bark.	Fibre little affected, solution yellow.	Fibre brownish-yellow, solution yellow.	Fibre little changed, solution yellow.	Fibre unchanged, solution yellow.
Flavin. . .	Fibre and solution yellow.	Fibre and solution yellow.	Fibre and solution yellow.	Fibre little affected, solution yellow.
Persian Berries.	Fibre unchanged, solution yellow.	Fibre orange-brown, solution greenish-yellow.	Fibre unchanged, solution brownish-yellow.	Colour slightly extracted.
Turmeric. . .	Fibre reddish-brown, solution colourless.	Fibre reddish-brown, solution brown.	Fibre bright reddish-brown, solution orange-brown.	Fibre bright reddish-brown, solution orange.
Annatto. . .	Little affected, or brownish-red.	Fibre and solution blue.	Little affected.	As with NaOH
Iron Buff. .	Fibre straw-yellow or decolorised.	Little action.	No action.	No action.
Chrome Yellow.	Fibre decolorised, solution pale yellow.	Fibre greenish-yellow or dull yellow.	Fibre paler, liquid pale yellow.	Little action.

COLOURS (*continued*).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre little affected, solution yellow.	No action.	With HNO_3 fibre light brown. Heated with Fe_2Cl_6 fibre becomes olive. Colour becomes orange by boiling with lead acetate.
Fibre brownish-yellow, solution bright yellow.	No action.	With HNO_3 fibre dark brown. Heated with Fe_2Cl_6 fibre becomes olive. Boiling acetic acid gives yellow solution with green fluorescence. Colour becomes orange by boiling with lead acetate.
Fibre brown, solution yellow.	No action.	With HNO_3 fibre brown. Heated with Fe_2Cl_6 fibre becomes olive. Colour becomes orange by boiling with lead acetate.
Fibre reddish-brown, solution colourless.	Colour extracted, solution orange or yellow with green fluorescence.	With HNO_3 fibre pale yellow. Boracic acid added to HCl and alcoholic solution, gives bright red colour.
Decolorised.	Solution bright yellow.	Dyed blue with K_3FeCy_6 + HCl.
Decolorised.	No action.	Fibre blackened with ammonium sulphide or H_2S.
Decolorised.	No action.	

GREEN

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Malachite Green.	Fibre and liquid bright orange; on washing with water the green colour is restored.	Fibre much bleached, liquid bright orange.	Decolorised.	Decolorised.
Methyl Green. (BASF)	Fibre and liquid pale yellow; colour restored on washing.	Fibre much bleached, liquid colourless.	Decolorised.	Decolorised.
Acid Green. (Soc. Chem. Ind.)	Fibre pale green.	Fibre brown, liquid yellow.	Decolorised.	Decolorised.
Alkali Green.	Fibre dark olive-green, solution reddish-brown.	Fibre and solution dark brown.	Decolorised.	Decolorised.
Helvetia Green	Liquid yellow; green colour restored on diluting with water.	Decolorised.	Fibre buff-yellow.	As with NaOH.
Cœruleïn. (BASF)	Fibre duller green, liquid claret-red.	As with HCl, liquid dirty amber yellow.	No action.	No action.

COLOURS.

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre almost decolorised, liquid yellow.	Green colour extracted.	Heated to 100° C. colour does not change to bluish-violet. (Distinction from Methyl Green.)
Fibre almost decolorised, liquid yellow.	Bluish-green colour extracted.	Heated to 100° C. becomes bluish-violet. (Distinction from Malachite Green.)
Fibre almost decolorised, liquid yellow.	Green colour readily extracted.	
Fibre not changed, bluish-green colour extracted.	Green colour extracted.	
Almost completely decolorised.	Bluish-green colour extracted.	
Fibre brownish-red, liquid brown; on washing with water colour gradually restored.	No action.	HNO_3 gives a brown spot.

GREEN COLOURS

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Aldehyde Green.	Fibre bright yellow.	Fibre orange.	Little action, fibre afterwards paler.	At first little action, afterwards bleached.
Vat Indigo and Old Fustic.	Fibre paler, liquid blue.	As with HCl.	Fibre greenish-blue, liquid yellow.	Fibre paler or blue, liquid yellow or greenish.
Vat Indigo and Chromate of Lead.	Yellow removed at once, blue afterwards; liquid dull yellow.	Fibre dirty yellowish-green.	Yellow removed; liquid pale yellow.	No action.
Indigo Carmine and Picric Acid.	Fibre at first blue, afterwards very pale; liquid blue.	As with HCl.	Fibre almost decolorised, liquid pale yellow.	As with NaOH.
Chrome Green.	No action.	No action.	No action.	No action.

BLUE

Alizarin Blue. (BASF)	Fibre violet, liquid yellowish-red.	Dilute H_2SO_4; fibre violet, liquid slightly red. Concentrated H_2SO_4 gives violet liquid.	Fibre bluish-green.	No action.

(continued).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Slowly decolorised.	Green colour extracted.	HNO_3 gives a brown spot.
Fibre much paler, liquid greenish-yellow.	See indigo.	Boiling glacial acetic acid gives green solution; on diluting with water blue is precipitated. Boiling $Al_2(SO_4)_3$ gives yellow solution with green fluorescence. Remove yellow colour by boiling with dilute Na_2CO_3, and test the blue remaining for indigo.
Fibre becomes at first blue, afterwards decolorised.	See indigo.	Ash contains lead. Blackened by $(NH_4)_2S$. Bleaching-powder solution changes colour to yellow.
Decolorised.	... ...	Cold water extracts Picric Acid, test solution with KCN.
No action.	No action.	Boiled with a solution of bleaching-powder gives yellow liquid containing chromate. Occurs only on calico prints.

COLOURS.

Fibre at first violet, on heating brownish-red, liquid is brown.	No action.	HNO_3 gives a bright yellow spot which goes brown after a time. Soap and bleaching-powder have no action. Phosphoric acid gives orange-red solution, which on diluting with water and adding NH_4OH becomes blue. A dilute ammoniacal alcoholic solution shows characteristic absorption stripes when examined with spectroscope.

BLUE COLOURS

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Soluble Blue. (B. S. & S.)	Extracts blue colour.	Fibre and liquid reddish-brown.	Fibre reddish-brown.	Decolorised at once.
Spirit Blue. (A. Poirrier)	Fibre dark green, solution brownish.	Fibre and solution reddish-brown.	Fibre brick red.	Decolorised slowly.
Alkali Blue 3 B. (BASF)	Fibre greenish-blue, solution almost colourless.	Fibre and liquid reddish-brown on standing.	Fibre at first reddish-brown, afterwards decolorised.	Decolorised rapidly.
Induline.	Fibre violet, liquid deep blue.	Solution dark blue.	Reddish-violet colour abstracted, the solution decolorised on addition of zinc powder. Violet colour restored by exposing filtered solution to the air.	As with NaOH.
Methylene Blue. (BASF)	Fibre nearly decolorised, solution bluish green.	Fibre and liquid green.	Fibre bluish-violet.	No action.

(*continued*).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre little changed, blue colour extracted.	*Absolute* alcohol, even on boiling, extracts no colour.	HNO_3 gives a dark spot, which changes to dark green with a black border.
Fibre not changed, liquid colourless.	*Absolute* alcohol extracts the colour, even in the cold.	HNO_3 gives a black spot, which changes to dark green.
Fibre not changed, liquid colourless.	*Absolute* alcohol extracts the colour, even in the cold.	HNO_3 gives a light green spot with black border.
Extracts a violet or green colour.	Bluish-violet colour extracted.	Induline NN is not changed by bleaching-powder solution. HNO_3 gives a dark bluish-green spot. Bleaching-powder solution changes some Indulines to a reddish-grey, whilst others are decolorised.
Decolorised.	Greenish-blue colour extracted.	HNO_3 gives a green spot which does not change further. Bleaching-powder solution turns it first green, and gradually decolorises it. *On cotton* it is much faster than aniline blues, and withstands neutral soaps, light, and weak bleaching-powder. Very sensitive to chromic acid. A 3 per cent. solution of $K_2Cr_2O_7$ changes it first to violet and finally decolorises it. If it has been fixed with tannin a brown colour is left.

BLUE COLOURS

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Resorcin Blue.	... ...	Dilute H_2SO_4, no action.	Solution blue, with red fluorescence.	As with NaOH.
Indophenol Blue.	Fibre greyish-brown.	Fibre greyish-brown.	No action.	No action.
Vat Indigo Blue.	No action.	Dilute H_2SO_4, no action. Concentrated H_2SO_4 gives a blue solution.	No action.	No action.
Indigo Carmine.	Solution greenish-blue.	Solution blue.	Fibre greenish. On boiling with dilute NaOH colour abstracted, solution little coloured, but becomes blue on acidifying.	As with NaOH.
Prussian Blue.	No action.	No action.	Fibre brown on heating.	No action.
Logwood Blue.	Fibre red or brown, solution red.	As with HCl.	Fibre and solution purple.	As with NaOH.
Ultramarine Blue.	Decolorised.	Decolorised.	No action.	No action.

(*continued*).

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
... ...	... ...	
Decolorised.	Blue colour extracted.	Boiled with olive oil purplish colour is extracted.
On heating fibre becomes paler, solution greenish-yellow.	Boiling absolute alcohol gives blue solution, which on standing becomes colourless with separation of indigotin.	Chloroform extracts blue colour. Strong HNO_3 gives bright yellow spot. Indigo-dyed *cotton* if burnt gives off purple vapour, which can be condensed on a cold porcelain slab as a blue spot.
Fibre decolorised on heating.	Little or no colour extracted.	Colour extracted by boiling with dilute Na_2CO_3; silk or wool may be dyed in the acidified solution. Nitric acid gives yellow spot.
No action.	No action.	Ash contains iron. Concentrated nitric acid gives green spot. Boiled with NaOH, solution contains potassium ferrocyanide, on acidifying and adding Fe_2Cl_6 blue precipitate is obtained.
Fibre and solution at first red, afterwards brown.	No action.	If used for topping vat indigo blue, it can be removed by boiling with dilute HCl, the indigo being unaffected thereby.
Decolorised.	No action.	On burning fibre blue-coloured ash remains. Only met with on calico or woollen prints.

VIOLET

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Galleïn.	Fibre brownish-red, liquid amber-yellow.	As with HCl.	Colour of fibre bluer.	No action.
Alizarin.	Fibre and liquid dull yellow.	As with HCl.	Colour of fibre bluer.	No action.
Methyl Violet.	Fibre yellowish-brown, liquid amber-yellow; the violet colour restored on diluting with water.	As with HCl.	Fibre at first pale reddish-violet, afterwards decolorised.	Fibre pale lilac, nearly decolorised.
Benzyl Violet.	Fibre yellowish-brown, liquid amber-yellow; the violet colour restored on diluting with water.	As with HCl.	Fibre at first bluer, afterwards decolorised.	Almost decolorised, fibre pale bluish-lavender.
Perkin's Violet.	Fibre unchanged, solution bluish-pink.	Little or no action.	Fibre blue, colour restored on washing.	No action.
Naphthylamine Violet.	Fibre grey.	... ...	Little or no action.	... ...
Phenyl Violet, or Spirit Violet.	Fibre dark green, solution brownish.	Fibre and solution reddish-brown.	Decolorised.	Decolorised.

COLOURS.

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre crimson, liquid red.	No action.	HNO_3 gives a bright yellow spot. Bleaching-powder solution has no action.
As with HCl.	No action.	Destroy the colour by boiling with dilute HCl, wash and add NaOH ; the Alizarin remaining on the fibre is dissolved with purple colour.
Fibre green, but nearly decolorised on standing, liquid yellowish-green.	Colour extracted.	
Fibre bright green, liquid pale yellow.	Colour extracted.	
Fibre dirty brown, but not decolorised.	Colour extracted.	HNO_3 has no effect. Cl bleaches the colour slowly.
... ...	... ...	
Blue colour extracted; only decolorises slowly.	Colour extracted.	HNO_3 gives a green spot.

BLACK

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Aniline Black.	No action, or colour becomes greenish-black, restored by alkalies. Acid solution brownish.	As with HCl.	No action.	No action.
Logwood Black.	Fibre red or olive-brown, solution deep red.	As with HCl.	Solution purple.	As with NaOH.
Woaded Black.	Logwood colour removed, indigo not affected, and fibre remains blue.	As with HCl.	Logwood colour removed, indigo not affected.	As with NaOH.
Alizarin Black.	Fibre orange, colour restored with NH_3.	As with HCl.	No action.	No action.
Tannin Black.	Bleached to pale straw colour, steeping afterwards in NH_3, gives reddish-brown colour.	As with HCl.	Fibre brownish-grey or black.	No action.

COLOURS.

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
Fibre greenish-grey, colour restored by NH_3.	Boiling alcohol extracts a brownish-red colour.	Bleaching-powder solution changes colour to brownish-red. Several passages through a concentrated solution of $KMnO_4$ and oxalic acid alternately, decolorise it. Weak oxidising agents have no action.
Fibre violet or greyish-red, solution red, afterwards brown.	No action.	Ash contains iron or chromium.
Fibre becomes dirty greenish-blue.	As with indigo-blue.	First remove Logwood colours, etc., by boiling with dilute HCl, and test blue remaining for Indigo.
As with HCl.	No action.	Ash contains iron. Occurs only on printed calico.
Decolorised.	No action.	Ash contains iron.

BROWN

Colouring Matter.	HCl.	H_2SO_4.	NaOH.	NH_4OH.
Alizarin. . .	Fibre brownish-orange, colour restored by NH_3.	As with HCl.	Action slight, fibre bluer, liquid tinted blue.	Fibre unchanged.
Nitroalizarin.	Fibre paler, liquid yellow.	Fibre darker, liquid orange.	Fibre darker, solution colourless.	No action.
Catechu Brown.	Little or no change, solution pale orange.	Little or no change.	Little or no change.	Little or no change.
Camwood Brown.	Fibre red, liquid yellowish-red.	As with HCl.	Fibre and liquid purple.	Fibre purple, liquid colourless.
Peachwood Brown.	Fibre and liquid yellowish-red.	Fibre yellowish-red, liquid yellow.	Fibre purple, liquid cherry-red.	Fibre purple, liquid colourless.
Dyewood Brown.	Red or purple colour extracted.	As with HCl.	Little change, liquid tinged red.	Fibre unchanged, liquid tinged red.
Bismarck Brown.	Fibre reddish-brown, solution red.	As with HCl, but darker.	Fibre brownish yellow solution colourless.	Fibre unchanged, solution brown.
Phenyl Brown.	Colour extracted, solution brownish-red	... ...	Purplish-brown colour extracted.	Reddish-brown colour extracted.
Naphthylamine Brown.	Fibre brownish-yellow, solution orange.	... ...	... ...	Fibre yellow.
Manganese Brown.	Slowly decolorised.	No action.	No action.	No action.

COLOURS.

$SnCl_2 + HCl$.	Alcohol.	Other Tests.
As with HCl.	No action.	
As with HCl.	No action.	
Fibre becomes paler, solution colourless or orange.	No action	Ash contains chromium and sometimes copper. Colour more or less bleached by boiling solution of bleaching-powder.
Fibre and liquid cherry-red.	... ...	Occurs only on wool.
Fibre and liquid cherry-red.	... ...	
Fibre redder, solution reddish.	No action.	Ash contains aluminium and iron.
Fibre almost decolorised.	Red or pink colour extracted.	Boiling water extracts colour; boiling glacial acetic acid still more, with yellowish-green fluorescence.
Fibre reduced to pink, solution colourless.	Dark brownish-red colour extracted.	
Fibre purple, solution pale pink.	Solution bluish-pink.	
Rapidly decolorised.	No action.	Ash contains manganese.

COMPARISON OF THERMOMETER SCALES.

(*Approximate.*)

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
100°	212°	72°	162°	44°	111°
98	208	70	158	42	108
96	205	68	154	40	104
94	201	66	151	38	100
92	198	64	147	36	97
90	194	62	144	34	93
88	190	60	140	32	90
86	187	58	136	30	86
84	183	56	133	28	82
82	180	54	129	26	79
80	176	52	126	24	75
78	172	50	122	22	72
76	169	48	118	20	68
74	165	46	115		

Comparison of degrees Twaddell and Specific Gravity.

In order to change degrees Twaddell into Specific Gravity, multiply by 5, add 1,000, and divide by 1,000.

Example.—Change 168° Tw. into Specific Gravity.

168 × 5
840
1,000
1,000)1,840
1·84 Spec. Grav.

To change Specific Gravity into degrees Twaddell, multiply by 1,000, subtract 1,000, and divide by 5.

Example.—Change 1·84 Spec. Grav. into degrees Twaddell.

1·84 × 1,000
1,840
1,000
5) 840
168° Tw.

Measures of Length.

The **Metre**, the unit of length, is the ten-millionth part of a line drawn from the Pole to the Equator.

1 millimetre	=	$\frac{1}{1000}$th of a metre	=	0·03937 inches.
1 centimetre	=	$\frac{1}{100}$th „ „	=	0·39370 „
1 decimetre	=	$\frac{1}{10}$th „ „	=	3·93708 „
1 metre	=	as above	=	3·2809 feet.
1 decametre	=	10 metres	=	10·9363 yards.
1 hectometre	=	100 „	=	109·3633 „
1 kilometre	=	1,000 „	=	0·62138 miles.

Inch = 2·53995 centimetres.
Foot = 3·04794 decimetres.
Yard = 0·91438 metres.
Mile = 1609·32 metres.

Measures of Weight.

The **Gram**, the unit of weight, is the *weight* of a cubic centimetre of distilled water at 4° Centigrade.

1 milligram	=	$\frac{1}{1000}$th of a gram	=	0·0154 troy grains.
1 centigram	=	$\frac{1}{100}$th „ „	=	0·1543 „
1 decigram	=	$\frac{1}{10}$th „ „	=	1·5432 „
1 gram	=	as above	=	15·4323 „
1 decagram	=	10 grams	=	154·3235 „
1 hectogram	=	100 „	=	3·5291 oz. avoirdupois.
1 kilogram	=	1,000 „	=	2·20462 lbs. „

Pound (avoirdupois) = 453·59 grams.
Ounce (avoirdupois) = 28·34 „

Measures of Capacity, dry and liquid.

The **Litre**, the unit of the measures of capacity, dry and liquid, is the *volume* of a cubic decimetre.

1 millilitre	=	$\frac{1}{1000}$th of a litre, or 1 cubic centimetre	=	15·432 grain measures, or 0·06103 cubic inches.
1 centilitre	=	$\frac{1}{100}$th of a litre	=	0·61027 „ „
1 decilitre	=	$\frac{1}{10}$th „ „	=	6·10270 „ „
1 litre	=	as above = 1000 cub. cent.	=	1·7608 pints.
1 decalitre	=	10 litres	=	2·2009 gallons.
1 hectolitre	=	100 „	=	22·0097 „
1 kilolitre	=	1,000 „	=	220·0967 „

A gallon of water weighs 10 lbs. (avoirdupois).

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