Dr Alexander Crum Brown
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ON

THE COTTON FIBRE,

AND ON THE

MANNER IN WHICH IT UNITES WITH COLOURING MATTER.

[COMMUNICATED TO THE CHEMICAL SOCIETY.]

BY

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By WALTER CRUM, F.R.S.

In the year 1843 I published a Memoir* on the manner in which cotton fibre unites with colouring matter in the process of dyeing. I endeavoured to show that the combination which there takes place is not the result of chemical affinity, as was at that time universally understood, but that the union is a mechanical one; and, among other illustrations, I described various processes of dyeing in which the mechanical union is in different ways effected.

Since that period much has been said in opposition to the views then advanced, but generally with a very imperfect apprehension of them. I had indicated but a few of the facts which led to the conclusions then arrived at, leaving unexplained other facts and processes which have been supposed to contradict them.

The subject is sufficiently important to demand the more full and systematic statement on which I propose now to enter,—repeating, necessarily, some of the illustrations formerly adduced, and taking advantage at the same time of certain new facts with which I have since become acquainted. In this way I conceive I shall best answer the particular objections, and correct the misstatements that have been made. I shall describe the processes to be alluded to in such a manner that the chemist who may not hitherto have attended to this technical branch of his science will have no difficulty in following the statements; and, from the new light in which the subject is viewed, I trust they will not be without interest, even to those who are already acquainted with the facts hitherto made known.

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* "Proceedings of the Philosophical Society of Glasgow," i., 98. "Phil. Mag.," vol. xxiv., April, 1844. "Ann. Ch. Pharm.," lv., 220.

In my original communication I gave a slight history of the old mechanical and the chemical explanations of dyeing. The early views entertained by Macquer, Hellot, and Le Pileur d'Apligny, with their theory of pores, incomplete and inconsistent as they were, and wanting the support of facts which we now possess, gave way at once to the chemical theory of Bergman. In his treatise on indigo, in 1776, that chemist attributed to cotton the power of elective attraction, which had just been promulgated for acids and bases, and in this reasoning from analogy he was followed by Macquer, Berthollet, and all other writers on the subject. But no one who is at all conversant with the rationale of the processes of dyeing, and with the laws of chemical combination as they are now understood, can examine the question without arriving at an opposite conclusion.

Cotton wool in the bleached state—that is, when freed as much as possible, by the action of alkalies, hypochlorites, and acids, from foreign ingredients—may be considered as pure woody fibre, or cellulose $C_{12}H_{10}O_{10}$. It is one of the most inert of vegetable bodies. In the textile fabric it is capable of having incorporated with it, in all proportions, a multitude of different substances, without changing its own or their physical or chemical characters, except by holding them against mechanical efforts to wash away, or otherwise to separate them, but yielding them up to their proper solvents as readily as they could be taken from a surface of glass—itself remaining unchanged.

We know only two examples of chemical combination into which cotton wool, without total disintegration, is capable of entering;—these are its compounds with nitric acid and with potash or soda. When cotton wool is made to imbibe nitric acid by the gun-cotton process, a true chemical combination is formed, in equivalent proportions, but the characters of both constituents are completely changed, and the cotton $C_{12}H_{10}O_{10}$ has, as I find, 3HO replaced by $3NO_5$, forming the compound $C_{12}H_7O_7$, $3NO_5$*. Or the substitution may be stated thus:—

$$C_{12}H_{10}O_{10} + 3NO_5 = 3HO + C_{12}H_7(NO_4)_3O_{10}$$

The combination with soda in mercerized cotton, if it does exist, is not so stable, and the ultimate constituents of the cotton

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* I have been represented, by Messrs. Porrett and Teschemacher ("Mem. Chem. Soc.," iii., 261) as taking a mechanical view of the nature of gun-cotton, but I can-

undergo no change; but, according to Dr. Gladstone, there is a chemical combination $C_{24} H_{20} O_{20}$, KO, which, although decomposible by water and by carbonic acid, resists washing with alcohol. All other substances with which cotton has been made to unite, including those which form its various dyes, retain the colour, and all the other properties which they possessed in a separate state. Their union does not materially affect even the degree in which they resist the external influences of light, or of alkaline and other re-agents.

The attraction which is attributed to porosity or capillarity we know to be an attraction of surface; but it is one in which, in consequence of its structure, the absorbing body has its power of attraction for that which it imbibes immensely increased. The term capillarity gives but a faint idea of the disproportion between the extent of surface of the cell which constitutes a pore in the woody fibre and the almost mathematical line or point of matter which that cell is capable of containing. From the experiments of Saussure, we learn that boxwood charcoal absorbs a quantity of carbonic acid 56 times greater than the capacity of its pores, which implies the existence of a large proportion of it in the liquid state. Other porous bodies have similar properties: raw silk, linen thread, the dried woods of hazel and mulberry, although they were found to condense but a small quantity of carbonic acid, took up 70 or 100 times their bulk of ammoniacal gas; and Saxon hydrophane, which is nearly pure silica, absorbed 64 times its bulk of that gas. The gas does not enter into combination with the solid which absorbs it: the air-pump alone destroys their union.

The power which charcoal possesses of attracting to its surfaces certain solid bodies which are dissolved in water is equally well known. Bone charcoal removes the colouring matter from the brown solution of tartaric acid, and from syrup in the refining of sugar. It precipitates lime from lime-water, and metallic oxides from their solution in ammonia or caustic potash; but no chemical

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not discover on what grounds. In my paper on the Nitrates and on Gun-Cotton ("Proc. Phil. Soc. of Glasgow," ii., 163, April, 1847. "Phil. Mag.," vol. xxx., June, 1847. "Ann. Ch. Pharm.," lxii., 233) I assign to it the constitution in the text, as the result of my own experiments. I have always attributed the difference between my analyses of gun-cotton and those of others to the purifying process to which, in the former case, the cotton was subjected.

union has ever been supposed to exist between the charcoal and these gases or solid matters. It is well known to be chemically indifferent to all such bodies.

Mitscherlich calls the force which produces such remarkable effects upon the gases an action of contact, or an attraction of surface, and he calculates the extent of surface, in proportion to the mass which it attracts, as a measure of the force which it exerts. But it is something more, or, at least, the fact may be more strikingly stated. The same, or even a larger amount of surface unenclosed, does not exert an equal power. Saussure, in his valuable paper on the absorption of gases, informs us that charcoal from boxwood in the solid state absorbs twice as much common air as when reduced to powder. The condensation of gases in the solid charcoal goes on, he conceives, in the narrow cells of which it is composed, and is analogous to the rise of liquids in capillary tubes. But when we pulverize a body containing such cells, we open and destroy a large portion of them. While, therefore, we increase the actual amount of surface, we increase in a much larger proportion the amount of the fluid on which it acts, and thereby diminish the intensity of the action.

It was these remarkable facts, as described by Saussure, Graham, Bussy, Mitscherlich, and others, and not the crude mechanical theories of the last century, that drew my attention to the similarity of the action of cotton-wool in several of the processes of dyeing.

The cotton fibre was first figured and published by Mr. Thomson, of Clitheroe, in 1834, in his interesting work on the "Mummy Cloth of Egypt," from drawings by Mr. Bauer.* These drawings gave an idea of the flax and of the ripe cotton fibre sufficiently true for Mr. Thomson's purpose; but in many respects they were most inaccurate. When, some time afterwards, the defects were pointed out to Mr. Thomson, he employed Mr. Varley, of London, again to subject these fibres to the microscope, and have figures of them engraved, intending, besides, to write a continuation of his memoir on the mummy cloth. This he did not live to complete, but some engravings were made, and published in No. 2 of the "Classical Museum," together with a copy of the first paper. Mr.

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* "Annals of Philosophy," for June, 1834, and "Ann. Ch. Pharm.," for January, 1849, lxix., 128.

Bauer represented the cotton fibre in the unripe state as a perfect cylindrical tube; and, when ripe, as a hollow cylinder collapsed longitudinally in the middle and twisted.

The mature cotton fibre is an irregular, partially twisted stem, of about $\frac{1}{1000}$th of an inch at its greatest diameter; and if we take the middling American at $1\frac{1}{4}$ inch long, a cord of $\frac{1}{8}$-inch diameter and 13 feet long would give an idea of its relative dimensions. It is not, however, of equal thickness. Towards the end farthest from the seed it gradually diminishes, in many cases, like the tape-worm, to about one-fifth of its greatest diameter; and there its form is cylindrical and straight. In other cases the tapering is not nearly so great. The apex is always rounded and closed.

Under the microscope the walls of these tubes do not exhibit openings of any kind which can be taken for lateral passages; but it is a well-known property of vegetable membrane that fluids pass through it with great facility, though no visible pores or apertures can be detected in it.

Substances applied to cotton as dyes, or for the purpose of attracting dyes, become fixed in the cotton fibre in two different ways.*

I. They are attracted and precipitated from their solutions by the pores of the cotton. Or,

II. They enter these pores in combination with an acid or other solvent, and in a state of solution; and are there fixed, not by an effect of porosity, but by the subsequent removal of their solvent, or by other means which render them insoluble in water.

Class I.—Attraction by Porosity; or, processes depending essentially upon attraction of surface. I shall describe, as an example,—

The Indigo Dye.—When a pound of finely divided indigo, mixed with a hundred and fifty pounds of cold water, is kept for some time in contact with hydrated protoxide of iron and quicklime, the indigo is gradually dissolved, and there is formed an olive-yellow solution, from which the indigo may be reproduced and

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* Pigments and other colouring matters which are fixed upon cotton by means of albumen, oils, &c., are not here treated of.

precipitated in its original blue state by oxidation, through exposure to the atmosphere.

When a piece of cotton cloth is immersed in a solution of any salt, or other substance which is indifferent to it, the solution is imbibed by the ordinary hydrostatic capillary force; and when the cotton is withdrawn, the same quantity of salt adheres to it whether the period of immersion be long or short. But when a similar piece of cloth is dipped in the solution of indigo just described, there is also exercised a power of decomposition and precipitation by which the indigo is gradually attracted to the cotton from the solution around it, so that, if the immersion be continued for a quarter of an hour, it becomes loaded with ten times as much indigo as another piece which has been withdrawn immediately after its immersion. If successive portions of cotton be employed, the solution becomes robbed in this way of all its indigo. Before exposure to the atmosphere (which, by oxidizing, restores its blue colour) the indigo is attached to the fibre in its yellow insoluble state.

The force here exerted appears to be analogous to that which enables charcoal and dried wood to precipitate bodies in similar circumstances; and there seems no greater reason for supposing that a chemical union has taken place in the one case than in the other.

Other examples of the first class will be given after the second has been described.

Class II.—Processes where the mordant or dye has entered and become fixed within the fibre, independently of attraction. *Example:* Madder colours, with mordants of acetic solutions of iron or alumina.

It is proper here to premise that no substance can be made to adhere effectively to cotton which has not originally been applied to it in a state of solution. However impalpable the insoluble powder or the precipitate which we employ, mixing it with gum or other mucilage, and so placing it upon the cloth, it cannot be fixed;—the washing which removes the gum removes also the insoluble matters which accompanied it.

The substance which produces the madder purple colour upon cotton is a lake, or black substance, which by great attenuation becomes purple. Being insoluble in water, it cannot, as we have seen, be made, ready formed, to attach itself to cotton. But it is composed of two ingredients—viz., oxide of iron, which can be dissolved in water by the intervention of an acid, and the colouring (or rather colourable) matter of madder, which is itself soluble in water. The method is, first to apply the iron in solution, and when that is rendered insoluble in the fibre, to place it in the solution of madder, which, passing also through the membrane, comes in contact with the iron within, and there forms with it the insoluble compound.

The iron employed in this way to attract the dye-stuff is called a mordant. Metallic iron dissolved in pyroligneous acid is the particular preparation used as a mordant for a madder purple dye. It is essentially an acetate of protoxide of iron. When a solution of this salt is applied to cotton, it is received into the pores of that body by common capillary attraction; but its oxide is not appropriated by the fibre, as indigo is. A stream of water being sufficient to remove it, it is evident that cotton has not the power of separating the protoxide from its acid, even when that acid is the acetic. But if, after the solution of pyrolignate of iron has been applied to the cotton fabric, it be allowed to dry, and then exposed to an atmosphere slightly warm and moist, the acetic acid gradually escapes, in proportion as oxygen is absorbed, and the iron, in the state of an insoluble hydrated peroxide, remains.

But as insoluble matters cannot pass into the interior of the fibre from without, so, when a substance has once entered that fibre or its pores in a state of solution, and has become precipitated within these enclosures, it is equally impossible for the precipitate to return. It is entrapped within the body of the fibre, or its tissue, and becomes fixed there.

It will be seen that this precipitation and imprisonment of the oxide is no case of attraction, either chemical or mechanical. It is a case of chemical decomposition, in which the cotton acts the part only of a vessel to receive the materials. The same solution, spread thinly over glass, and placed in similar circumstances, undergoes the same decomposition. The greater subdivision of the salt may, indeed, in the case of the vegetable fibre, accelerate its decomposition; but a slight elevation of temperature in the other case is sufficient to compensate for the greater exposure in the cotton fibre.

The inferences that may be drawn are,—

1*st.* That the pores, whether larger or smaller, receive the solution of iron by ordinary hydrostatic capillary attraction.

2*d.* That while within these cavities or vessels, whatever be their form, the salt is peroxidized and decomposed; and

3*d.* That the result of the decomposition—an insoluble oxide—is left there by the volatile acid, which, by its solvent power, had enabled it to take that position.

In pursuing the process, the cloth which is thus furnished with its mordant of iron is first passed through hot water, with certain precautions which need not here be detailed, and washed, to remove any unfixed mordant; after which it is ready to be dyed. For that purpose it is made to traverse for a couple of hours a vessel of water, throughout which madder in powder has been distributed. Heat being gradually applied, the colouring matter of the madder dissolves, slowly indeed, and by little at a time, but, being soluble, it has no difficulty in passing into the fibre which encloses the oxide of iron, and there uniting with it. The resulting compound is the purple lake.

This last step of the process is a purely chemical one, in which the oxide of iron forms a true combination with the colourable matter of the madder, the cotton attenuating the iron to a prodigious extent, and placing it in circumstances the most advantageous for forming a lake with this dye-stuff.

Having thus received the dye, the fabric is subjected to a process of soaping in boiling water, by which its colour is much reduced in depth and brightened in shade.

Having formed the idea that no portion of the dye but that which is held most firmly within the cotton fibre could bear the severe soaping operations to which this class of prints is subjected, I formerly described a piece of dyed cotton as consisting of a set of colourless bags, containing coloured substances, and in so far resembling the cells of natural flowers; but the statement was incomplete, and the proof rested to some extent upon theoretical considerations, until the opportunity occurred of observing the effects of the same process upon "*dead cotton.*" And as the behaviour of this substance, in such circumstances, throws much light upon the question we are now discussing, I shall proceed to give some account of it.

Dead Cotton.—In May, 1848. Mr. Thomson, of Primrose.

received from Mr. Daniel Kœchlin, of Mulhouse, some specimens of a purple-ground printed calico, each of them containing a portion of cotton which was white, although it had been subjected to the same treatment by which the rest of the cloth, and even the threads which crossed the white ones, were uniformly dyed. The white part of the thread was usually thicker than the rest, and little more than a quarter of an inch long. The whole fabric had been thoroughly bleached before printing, so that its white thread contained no grease or other impurity that could have mechanically resisted the mordant. Mr. Kœchlin at the time suggested that it might consist of unripe cotton, and might want the hollow of the perfect fibre. Both in France and in this country it is called "*dead cotton.*" Mr. Thomson kindly transmitted me the specimens for examination, and my first observations on the subject were published in 1849, in the "Proceedings of the Philosophical Society of Glasgow."*

On placing it under the microscope, I found the cotton which had thus resisted the dye to consist of very thin and remarkably transparent blades, some of which were marked or spotted, while others were so clear as to be almost invisible, except at the edges. These fibres are readily distinguishable from those of ordinary cotton by their perfect flatness, not having the vestige of a cavity even at the sides, and by their uniform as well as great transparency. They are broader than the usual fibre, and they show numerous folds, both longitudinal and transverse.

On afterwards searching among the motes, or hard portions, called droppings, which are rejected by the picking machine in the preparation of raw cotton wool for spinning, I found what proved to be the same fibre, in the form of a small matted tuft of a shining silky lustre, several of which enclosed the fragment of a seed, or perhaps an imperfectly formed seed. The fibres are short, and have little tenacity. Small tufts, however, do occasionally pass the sifting process of the picking machine; and then these fibres, being too short to be teased out in the carding engine, or properly drawn into threads in the subsequent operations of cotton-spinning, remain as minute lumps, or knots, entangled among the fibres of the thread of good cotton, giving great annoyance to the spinner of fine yarns, and appearing as white specks upon a woven and dyed fabric.

In the month of June, 1862, I was favoured by Mons. Le Play,

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* Vol. iii., p. 61; also "Philosophical Magazine," vol. xxxv., November, 1849.

at the request of Dr. Playfair, with a number of specimens of the dried fruit of the cotton plant in various stages of maturity, from the Algerian collection in the International Exhibition, and was thereby enabled to ascertain the real nature of the peculiar fibre.

1*st.* I found that the contents of every capsule which had not opened, and of those which had but slightly opened in drying after having been cut from the plant, consisted in each cell of a closely packed solid mass, without elasticity, which, however, could be teased out into fibres, presenting under the microscope the flat, glassy, broad appearance exhibited by the dead cotton fibre already mentioned.

2*d.* In capsules more fully developed, the ordinary cotton appeared where it had pushed its way outwards, and assumed the woolly form; while the seeds in the same cell nearer the calyx, and still confined, were clothed with the solid mass, chiefly consisting of the glassy though somewhat less transparent fibre.

3*d.* The glassy fibre frequently appeared in pods of ripe cotton, in spots where discoloration showed that an injury had taken place before maturity.

4*th.* Small portions, glazed and satiny, which proved to be dead cotton, though not discoloured, were seen, but rarely, on the outer part of the wool of a well-clothed ripe cotton seed.

5*th.* We must add to these sources of dead cotton the small glazed tuft already mentioned as found in cotton bales, and appearing to have separated from the stem through which it derived nourishment, while the other seven or eight seeds in the same cell went on to maturity.

6*th.* The glassy fibre is broader—often one-half broader—sometimes even twice as broad as the ripe fibre.

7*th.* A distinct gradation is perceptible under the microscope in different specimens, from the pure and spotless glassy fibre in the least mature cotton, to the comparatively dense and opaque ripe cotton.

I shall describe four of these varieties of the cotton fibre as they are found in the dried state in commerce. I shall afterwards describe their behaviour with mordants; and, in doing so, I have to acknowledge my obligations to my assistant, Mr. M'Farlane, for his valuable co-operation in the preparation of materials and dyes.

1. *Mature cotton.*
2. *A cotton which I shall call three-fourths ripe.*
3. *Half-ripe cotton.*
4. *The youngest cotton found in commerce.*

MATURE COTTON.

Plate I. gives a view of various forms of cotton fibre in a state of maturity, mounted dry, and magnified about 400 diameters. They have often been represented before, and are produced now principally that they may be compared with the unripe fibres shown in Plate II.

After numerous attempts, which were but partially successful, to observe the interior of the cotton fibre, I was enabled, by the instructions of Mr. Hennedy, of Glasgow, to procure in great perfection abundance of transverse sections, exhibiting in the most interesting manner the nature of its contents.

From the drawings of these sections in Nos. 1 and 2, Plate III., it will be observed that the cotton fibre is not a hollow tube or bag filled with air, as it has been hitherto represented to be, but a nearly solid stem, with a very small cavity in the centre. A few of these slices are nearly circular, representing cylinders, but the greater part are irregularly oblong or oval shaped, with a central marking or aperture of corresponding form. They resemble the *liber fibres* of hemp or flax, as these have been delineated by Mr. Tuffen West in the "Micrographic Dictionary."

UNRIPE COTTON.

The youngest or least ripe of the fibres of cotton, as it is imported, are those of the small glazed tuft found among the rejected portions of cotton wool in its preparation for spinning. They are identical with the white specks I have already often referred to, which occur upon dyed fabrics, and to which the name of *dead cotton* has been given. Plate II. contains specimens of these fibres, viewed lengthways and mounted dry. In glycerine jelly they appear still more transparent, and in Canada balsam they are scarcely distinguishable from the surrounding medium. At No. 8, Plate III., are transverse sections of the youngest fibres as mounted in glycerine jelly. They are so thin that they can only be made to stand upright where the section is bent. In many of them the sides adhere to each other so firmly that no line can be detected to mark a division between the walls, for even the rough treatment of the knife does not always serve to separate them. Others, however, have a slight mark between the two outlines, chiefly at the end of the section, and then they somewhat resemble the thinnest of the half-ripe fibre.

Plate II. contains also side views of the cotton which I propose to call *half-ripe*, or in the second stage of maturity, mounted dry. This is the wool contained in an Algerian pod pulled green, and slightly open when dry, and I have found it the most interesting of the unripe cottons for the purposes of this inquiry. No. 4, Plate III., shows the microscopic appearance of transverse sections of this half-ripe cotton mounted in glycerine jelly. A line is always to be observed in the centre, pointing out that the flat blade consists of two walls, and that it is a flattened bag or tube.

I have found a distinctly marked *third stage*, which I have called *three-fourths ripe*, in a pod of Orleans cotton of the same external appearance as the Algerian pod containing the half-ripe wool. The walls of this fibre are considerably and uniformly thickened, but the fibres themselves are comparatively flat, and none of them are cylindrical. It is represented in transverse section at No. 6, Plate III.

Commencing with the thin and flat blade (of dried cotton), whose section shows no apparent opening, the ripening of the fibre thus goes on, by the gradual thickening of its walls, until it assumes the more or less cylindrical and solid form of ripe cotton, exhibited in Plate III., Nos. 1 and 2. On first observing that fact, there did appear to me some authority for applying the generally understood principle of a formation of new and separate matter in the process of ripening; but I am inclined to doubt that explanation, after having observed that the substance of the thin wall, as it exists in the half-ripe fibre, and after being removed from the plant and dried, is itself, as I shall now relate, capable of expansion, so as not only to give the fibre the cylindrical form, but to fill up a great part of the interior of the cylinder.

Of the Half-ripe Cotton artificially Expanded.—When the half-ripe but still perfectly flat and thin dried fibre (No. 4, Plate III.) is soaked in a solution of caustic soda of specific gravity 1·300 or 1·400, it at once assumes the round solid form of ripe cotton, differing from the naturally matured fibre only in being smaller, more generally cylindrical, and in having a larger aperture in the centre. It is represented at No. 5, Plate III.

To produce this change, it is best to soak the unripe fibre in water before dipping it in the strong caustic soda, without which precaution it is apt to become matted together, and less fit for subsequent operations. After the soda, it is washed in water, then treated with a weak acid, and again washed.

It is well known that *mercerized* cotton, as the ordinary cotton wool when so treated has been called, retains, after washing, none of the alkali that had swelled it. The increase of magnitude which the half-ripe fibre thus acquires is due, therefore, altogether to an expansion of the cell wall, or a separation from each other of the inner and outer surfaces of that wall.

The youngest fibres do not seem to become rounded by caustic soda.

It may now appear not improbable that, by the natural process of ripening, an effect is produced similar in character to that which is given to the unripe fibre by artificial means, and that the natural expansion may be ascribed, not to the importation of a new kind of matter, coating the interior of the original cell wall, but to a strengthening and rendering elastic of the membrane already existing of the wall itself, so as to produce the separation from each other of the cells or laminæ, or other structure of which it must consist.

The singular effect of strong alkaline solutions upon cotton woven fabrics was discovered by Mr. John Mercer, and patented by him in 1850. From the transverse section of the mature fibre thus altered, as shown at No. 3, Plate III., it will be seen that the action of the soda completes the cylindrical form of that fibre, at the same time greatly enlarging its volume, and filling up almost entirely the central cavity. The twisting of the fibre is also much increased, as shown at B, Plate IV., and there is a consequent shortening of it, sufficient to account for the shrinking in length and breadth, and the thickening of any woven fabric which is made to undergo the mercerizing process. Diagonal lines are sometimes seen in these ripe mercerized fibres, giving the impression of a spiral structure; but they are evidently the creasing or corrugating effect of extreme twisting. Diagonal lines, apparently also from the effect of creasing, may occasionally be detected in the original flat unripe fibre, Plate II. They seem to cross each other where the two sides of the fibre can be viewed in the same focus.

I have made many attempts, by the use of Ross's $\frac{1}{8}$, and Powell & Lealand's $\frac{1}{25}$-inch object glasses, to discover how the wall is built up in the mature cotton fibre, but without success. Some concentric rings in cross sections, sketched in Plate VII., are apt to be mistaken for internal structure. They will be recognized as an optical effect, obtained by placing the illuminator out of focus, and especially when using gas-light.

Mordanting with the Acetates of Iron and of Alumina.

Plate IV., A, shows side views of the ordinary cotton fibre which has been made to imbibe the pyrolignate of iron in the manner described at page 7, and then dyed in madder and soaped. The compound of madder and iron which forms this purple dye is so uniformly distributed over the cellular matter which it colours, that we can scarcely detect any point of the full-grown fibre which it does not pervade. On the other hand, although the greater part of the dark markings of these fibres are due to irregularities of the surface, corresponding with those of the undyed fibres, Plate I., there are other markings to be found in the centre of almost every fibre, which, after examining the cross sections of the same preparation at D, Plate VIII., and observing the clots which occur in the centre of many of them, will readily be recognized as accumulations of the black lake of madder and iron.

We must assume that in this process every cavity of the fibre has been filled with the iron solution, and we know that when that solution is evaporated to dryness, the acetate is gradually decomposed and converted into the hydrated peroxide of iron, which, by combining with madder, becomes the black or purple lake already alluded to. The cavity in the centre (D, Plate VIII.) is sufficiently capacious, and admits solution enough to exhibit to us this lake in the form of a bulky black clot collected into one mass, altogether separate from, and sometimes scarcely touching the bag which contains it. It is not too much to infer that, in each of those innumerable though invisible cavities which exist throughout the body of the fibre, a similar process goes on, and that each enclosure, after imbibing its fill of the iron solution, contains first a parcel of the dried acetate, which soon becomes a clot of the hydrated peroxide, as distinct in its degree from the wall which surrounds it as that which we are enabled to see in the central cavity. I need not repeat that the substance which is seen under the microscope to be black in the central opening is the same with that which, in a state of still greater subdivision, gives a purple colour to the body of the fibre. At B, Plate IV., and at E, Plate VIII., are shown the effects of the same process applied to mature cotton previously mercerized. When acetate of alumina is employed, instead of the iron solution, the only difference in the appearance is the substitution of red for purple.

Plate VI., No. 1, shows transverse sections of the ordinary cotton fibre mordanted with acetate of alumina and dyed red. In depth of colour they are extremely unequal, of which the chief cause, no doubt, is the variety in the thickness of the slices; but there are always present also fibres comparatively unripe; and even well-formed fibres differ in the amount of the colour they receive. This inequality is nowhere more remarkable than in the cross sections and the side views of the most beautifully dyed turkey-red yarn, notwithstanding its perfectly uniform appearance to the naked eye in the aggregate.

Deep red specks, which are evidently clots of the red lake of alumina and madder, are seen occasionally occupying the otherwise void space in the heart of the fibre mordanted with acetate of alumina; but these occur to a much greater extent in cotton mordanted with mono-muriate of alumina, as will presently appear.

No. 2, Plate VI., shows the appearance of a fibre mordanted with acetate of alumina, and not fully dyed—that is, a fabric to which a sufficient quantity of madder had not been given to saturate all the alumina which it had received. It is only as the outer portions of the mordant become saturated that they allow the madder to pass inwards; and until that takes place the fibre remains uncoloured in the centre.

Whether Thickening impedes the Entrance of a Mordant into the Cotton Fibre.—I shall here remark, that whether the mordant be applied to a piece of calico in the fluid state, or made nearly solid with an amylaceous or other thickening substance, it finds no difficulty in traversing the whole fibre. I have examined threads which have been soaked with a solution of acetate of alumina altogether fluid—comparing them with other threads which had been printed with the same solution made into a thick mucilage with gum-arabic, and with others again made into a paste with the flour of wheat, so thick that when applied to one side of a piece of bleached calico it did not pass through to the other side; and on examining transverse sections of dyed specimens of these fibres, I found that such of them as had been reached by the mordant were in all these cases equally penetrated. The white centre was always due to a want of dye-stuff.

I am glad to be able to establish this fact—an apparent impossibility,—which has been a stumbling-block to several of my friends. It is difficult, no doubt, without direct examination, to conceive of a capillary power so great, or that a solution rendered so tenacious as to require considerable force to drive it through an opening of an inch in diameter, should be able, without any pressure at all, to pass into the interior of the cotton fibre, the pores of which cannot be detected by the most powerful microscope. In the latter case we have reason to believe that the solution leaves its farinaceous accompaniment at the entrance, and passes on; but a similar effect cannot be so readily supposed in the case of a mucilage.

Plate VII., B.—The *youngest fibre* bleached and mordanted with acetate of alumina, then dyed with madder, and afterwards soaped. A. The youngest fibre unbleached and similarly treated.

Plate V., B.—The *half-ripe fibre* unbleached, mordanted with acetate of alumina, dyed with madder, and soaped. When bleached, a great many fibres of the half-ripe cotton remain altogether colourless after having undergone the dyeing process, and the whole are much paler than the unbleached. C. The same half-ripe fibre bleached and mercerized, and then similarly treated.

The fibre *three-fourths ripe*, whether bleached or unbleached (judging from the small specimen at my command), takes a dye, after mordanting with acetate of alumina, little, if at all, inferior to the mature cotton.

MORDANTING WITH MONO-MURIATE OF ALUMINA.

To prepare this solution, the sulphate of alumina (known as concentrated or cake alum) is decomposed by chloride of calcium, and the fluid purified from iron by means of ferro-cyanide of potassium. For that purpose a solution of the ferro-cyanide is added to the impure muriate of alumina so long as any precipitate is formed; and as the deposit does not separate by filtration, it is left to subside. Small floating particles, however, remain after the principal part of the prussian blue has gone down, and these are separated by albumen, a very small quantity of which collects them in the usual way of clarifying. The product is then divided into three equal parts. Two are decomposed by ammonia, and the precipitated alumina, after being filtered and washed, is added to the third portion, which re-dissolves it.

The mono-muriate of alumina thus formed has usually been employed for these experiments of a specific gravity 1·125, at which it is strong enough to be converted into a thick magma by the addition of ammonia. The cotton is left to soak several hours in this solution, after which it is washed in water, dyed in madder, and soaped. I shall describe the action of this compound upon the various fibres more particularly than its industrial importance would seem to merit, because it represents what appears to me to be an additional character not before recognized in the action of mordants upon cotton.

The Youngest Fibre, when bleached, takes no alumina from the solution of the mono-muriate. I have given a sketch, however (D, Plate VII.), for comparison, of fibres which have been subjected to the process. The same fibre unbleached (C, Plate VII.) takes exceedingly little. Many of the unbleached fibres remain destitute of colour, and others, probably more mature, take up a very small quantity of alumina, and they all take it in the peculiar way there represented—a layer of alumina between the walls of the fibre.

It is the cotton, however, in what I have called the *half-ripe stage,* that furnishes the most remarkable example of the peculiar manner in which alumina is deposited in the fibre by immersion in the basic solution of that earth. I have endeavoured to picture its microscopic appearance in Plate V., A, the flat fibres being the same as those shown without dye in Plate II. The same preparation is represented in transverse section, Plate VI., No. 7. Unlike the youngest fibre, the half-ripe cells are in such a state of growth that their walls readily separate to admit of the introduction of the fluids in which they may be immersed. When after two or three hours of such immersion the cotton is washed in cold water, a quantity of hydrate of alumina is found separated from its solution, and retained by the fibre.

The circumstances are these:—The young fibre, an empty flattened bag, is placed in the basic solution, which soaks and more or less completely fills it. It is then put into water, or what Mr.

Graham has called an atmosphere of water. The bag or cell wall acts the part of the septum described by him in experimenting on similar fluids, and the salt is decomposed. The crystalloid portion—the muriate of alumina—diffuses through the septum into the surrounding water, and the colloid hydrate of alumina remains within, gelatinized, no doubt, either spontaneously or by the traces of saline matter which are always present. The fibre itself, through which the aluminous solution has passed and repassed, retains no trace of the presence of alumina. It may be called a microscopic dyalizer.

Many of these fibres seem as if a thin film of alumina had originally been deposited within them over their whole length and breadth; and in all of them there is evidence of the deposit having shrunk to a great extent in both directions in the process of dyeing. It is remarkable that the alumina should adhere so slightly to the membrane which contains it as thus to shift without difficulty from one part of it to another in the act of shrinking. The same remark applies to the clots found in the centre of full-grown cotton, whether the mordant of iron or alumina be applied from an acetic solution, or as in the case before us.

By previous bleaching of this fibre the quantity of alumina which it can receive is much diminished; but enough is admitted to form with it a most interesting microscopic object. In all cases the cell remains beautifully colourless and crystalline, enclosing its flakes of carmine; and the variety in the distribution of these flakes is infinite.

Along with these drawings are placed representations (D, Plate V.) of the same half-ripe fibre in the unbleached state, and swelled out by strong soda, previous to receiving the mordant; and they form examples not less remarkable of the action of the cotton fibre upon this salt. The opening in the centre appears to have been entirely filled with the clot, which (as it does with other fibres) has shrunk both in length and breadth in the subsequent processes. In the corresponding transverse sections (Plate VI., No. 8) pieces of the clot may often be seen scattered over the slide, having dropped out of their places, and lying near the aperture which had contained them.

When the half-ripe cotton is bleached previous to being mercerized, and then mordanted with mono-muriate of alumina and dyed (E, Plate V.), not only is the body of it much paler than the unbleached, but no such masses of colour reach the centre. In some instances a colourless fibre encloses a quantity of the red lake.

The effect of bleaching, in diminishing the power of cotton to receive mordants, is to be attributed to the boiling in weak solutions of quicklime and carbonate of soda to which the cotton is subjected, and not to the hypochlorite of lime, which is very sparingly used in the process of bleaching, nor to the sulphuric acid, which does not affect the mordanting. Hot alkaline solutions, though weak, mat together the young fibres, and close their passages against the admission of mordants. They have a similar tendency when applied to riper cottons, while that of strong caustic alkaline solutions is, as we have seen, to open them. Hypochlorites in excess also open the pores of ripe cotton, and, by enabling them to admit more mordant, greatly increase the intensity of the dye.

At No. 3, Plate VI., are cross sections of ordinary cotton, mordanted with mono-muriate of alumina. Like the unripe fibres, they show that the salt had passed into the centre of the tube, and had been there decomposed.

MORDANTING WITH OXYCHLORIDE OF IRON.

The sesquichloride of iron, with the addition of an equivalent of sesquioxide of iron, forms a solution ($Fe_2 Cl_3 + Fe_2 O_3$) corresponding, in its action upon the cotton fibre, with the mono-muriate of alumina. It gives up its peroxide in a similar manner, and thus forms a mordant which, when dyed with garancine, produces upon the cotton a black or a purple colour, in proportion as the quantity of oxide which it has received is greater or smaller.

The oxychloride may readily be obtained by adding ammonia to 100 parts by weight of nitrate of peroxide of iron of specific gravity 1·55, washing the precipitate, and re-dissolving it in 37½ parts hydrochloric acid of specific gravity 1·17.

The cotton is steeped for a couple of hours in this solution reduced to the specific gravity of from 1·03 to 1·07; after which it is placed in water, and washed before being dyed. The dye for this preparation of iron is garancine, and it does not require soaping.

The effects are shown in Plate VIII. The unripe fibre, A and A_2, acts the part of a membrane or dyalizer for decomposing the solution when placed in water, and as a bag for retaining (without being itself coloured by) the precipitated oxide, or its purple lake. The same fibre, B and B_2, while it has an equal power of admitting the solution into its interior, has likewise, by the mercerizing process, had cavities or enlarged pores formed in its wall; and each of these appears to have taken its proportion of the iron, so as to produce, when dyed, a purple tube—the larger quantity of iron in the centre giving a black. With the ripe fibre, C and C_2, a quantity of the oxide has been retained in the hollow centre, and but little by the walls themselves.

I shall now enumerate a few additional processes which belong to the two different classes, of which I have already given examples.

Class I.—A. The indigo dye has been already described as the type of those which cotton attracts by its porosity.

B. Bodies, such as safflower, turmeric, &c., which, like indigo, are colours *per se*.

C. Bodies which, while they attach themselves to cotton as indigo does, are not, like indigo, possessed of colour, but have the power of attracting and uniting with other bodies, and of forming with them coloured compounds.

a. Tannin is much employed in this way. When cotton is immersed for some time in a warm decoction of gall-nuts, or in a solution of tannic acid, a considerable quantity of tannin is deposited in the fibre; and if cloth so charged be subsequently immersed in the solution of any metal with which tannin is capable of uniting, it is attracted and deposited along with it in the fibre. In this way a black dye is often produced with nitrate of iron. The metallic solution becomes in that case the dyeing material, and the vegetable body the mordant. Tannin attracts also the violet colouring matter of Perkin.

b. Oxide of lead is readily fixed upon cloth on the same principle. The cotton fibre, by mere immersion in the fluid, separates lead from its solution in lime or in soda, as charcoal does; and when cloth so loaded is treated with a chromic salt, a yellow chromate of lead, or an orange dichromate, is produced. By treating leaded cloth with protosulphate of iron, we obtain, instead of oxide of lead, a deposit of peroxide of iron and sulphate of lead; and if the sulphate, by immersion in ammonia, be reconverted into oxide, it becomes capable of fixing another equivalent of iron, and so on as often as we alternate the immersions in ammonia and sulphate of iron. It is remarkable that leaded cloth attracts scarcely any iron from the red salts of that metal.

D. Bodies which form mordants for attracting and uniting with other mordants.

a. Tannin fixed in the manner just described is employed to attract tin from an acid solution of tin, and in this way a compound mordant is produced which is the most suitable, by subsequent dyeing in Lima or Brazil wood, for producing what is termed a fancy red—a dye at one time much used as an imitation of turkey-red.

b. As subsalts of iron by themselves do not advantageously deposit their excess of oxide in the cotton fibre when it is immersed in their solutions, the intervention of tin is employed. When cotton is soaked in a cold and weak solution of oxychloride of tin, or still better, in a mixture of the bichloride and protochloride, and when, after this preparation with tin, it is immersed in oxychloride or oxynitrate of iron, a large quantity of iron is deposited, in the state, I presume, of a stannate of iron. This mordant, when dyed in ferro-prussic acid, forms a prussian blue of the greatest richness and brilliancy.

VARIETIES OF CLASS II.—A. The acetate of iron has already been mentioned as an example of this class.

B. Acetate of alumina acts in a similar manner.

C. From the manner in which the mono-muriate of alumina acts upon cotton, it is evident that the process in which it is employed must also be placed in the 2*d Class*, as defined at page 5 of this memoir, and not in the 1*st Class*. The alumina is not attracted by the pores of the tissue, as indigo is. When dissolved in the termuriate, it passes into the interior of the fibre through these passages by ordinary capillary force, and when the fibre, with its contents, is subsequently placed in water, the alumina remains in its enclosure, in consequence of the diffusive character of its solvent.

D. If we wish to fix upon cotton other oxides, as those of copper, manganese, or chromium, which do not spontaneously, or by diffusion, part with the acids which dissolve and carry them into the fibre, we must employ an alkali to precipitate them there. The acetate and nitrate of lead being also not spontaneously decomposible, cotton which has been charged with these salts has to be treated with ammonia or a carbonated alkali, or a sulphuric salt, to fix the lead in the fibre. Aluminated potash is, in the same way, treated with sal-ammoniac; the stannate of soda, with weak sulphuric acid; the sulphates and chlorides of manganese and of iron, by caustic soda; the salts of oxide of chromium, by carbonate of soda, &c., &c.

E. Steam colours, where mordant and dye mix together without combining. The mixture, therefore, retains the solubility of its ingredients, and enters the fibre as readily as either would do in a separate state. Heating in steam of boiling water determines the union and consequent precipitation within the fibre where the mixture had been deposited. Decoctions of those vegetable colouring matters which form lakes with aluminous salts are chiefly here referred to.

F. Steam Prussian Blue. Ferro-prussic acid applied to cotton and subjected to steam causes a deposition of white proto-cyanide of iron, which is changed by the air into prussian blue.

I have thus endeavoured to illustrate two principles, on one or other of which dyes can alone enter the cotton fibre. But dyes are not always confined to the interior of the fibre. Previous to the soaping which follows the application of the madder in the madder-purple process, a considerable quantity of the dye remains less firmly fixed than the rest; and in the case of the numerous class of colours which do not require the soaping process, that external dye is allowed to remain. Most colouring matters would not bear so severe a cleansing; and, besides, much richness of hue and velvety aspect would be lost if a portion of them were not left to cover the fibre and its occasional imperfections. All that class of goods which are dyed with garancine,—the indigo dyes,—all colours fixed by steam, and, indeed, the great majority of all prints, are in this situation.

We can readily conceive of a tissue so subdivided as the cotton fabric having passages less perfectly enclosed than those we have been describing, and yet narrow enough to be capable of harbouring more or less securely such insoluble matters as may be left there by an iron or aluminous acetate, during its spontaneous decomposition, and even of exercising to some extent a capillary decomposing power over such a solution as that of indigo. We know, besides, that in many dyes part of the colouring matter is attached only by cohesion, for which the spaces between the fibres furnish ample opportunity. But all comparatively external adhesions, although of great commercial importance, are only superadditions to the greater amount of dye which is, or ought to be, in all cases fixed within the fibre, on one of the two principles which it has been my object to explain.

The "dead cotton" is still apparent in most of these dyes. I have observed it principally in the indigo dye, the chrome-orange dye, the aniline-violet fixed with tannin, and in the dyes from the iron and aluminous mordants where these are attached to the cloth by deposition from basic solutions of their salts. By that method of fixing iron and alumina, white specks appear which would not be discernible when the ordinary mordants are employed. But the "dead cotton" is also distinctly visible (more or less tinged) in all garancine dyes, whether chocolate, black, red, purple, or catechu, even when washing with water is the only means employed to cleanse after dyeing; and it appears in all steam colours that are well washed.

The "dead cotton" does not however refuse all colouring substances. On examining a safflower-pink dye, the "dead cotton" seems to have attracted its full proportion of it, and the same is the case with the prussian blue, which is produced from stannate of iron. By repeated dips in the indigo-vat, too, the "dead cotton" is concealed, if not otherwise dyed.

EXPLANATION OF THE PLATES.

PLATE

I. Full-grown cotton, magnified about 400 diameters, as seen with Ross's $\frac{1}{8}$-in. object-glass, and mounted dry.

II. Unripe cotton.—Half-ripe cotton taken from an Algerian pod, which, when dry, was almost entirely closed; and along with them fibres in what I have described as the youngest stage.

III. Transverse sections of various conditions of the cotton fibre, as there described, and all as they appear when mounted (except No. 2) in glycerine jelly.

IV. A, Full-grown cotton prepared with a mordant of pyrolignate of iron, then dyed in madder and soaped. At D, Plate VIII., will be found transverse sections of A.

B, The same as A, but steeped before mordanting in a strong solution of caustic soda. At E, Plate VIII., are transverse sections of B.

V. Half-ripe fibres with aluminous mordants, dyed in madder and soaped.

A, Mordanted with mono-muriate of alumina.

D, The same, but mercerized in the unbleached state before mordanting.

E E, The same, bleached and mercerized previous to mordanting.

B, Mordanted with acetate of alumina without being bleached.

C, Mordanted with acetate of alumina after having been bleached and mercerized.

VI. Transverse sections of the various fibres with aluminous mordants, dyed in madder and soaped.

VII. A and B, The youngest fibre mordanted with acetate of alumina, showing the effect of bleaching upon dead cotton in rendering it less capable of receiving a dye. C and D, which are mordanted with mono-muriate of alumina, give the same indication in an equally remarkable manner.

Transverse sections of mature cotton dyed chrome-orange, as seen with Powell & Lealand's $\frac{1}{25}$th inch, showing concentric rings—an effect of diffraction, not of structure.

VIII. A, The half-ripe fibre mordanted with oxychloride of iron, and dyed with garancine. A_2, Transverse sections of A, where the greater part of the lake is seen to be lodged in the hollow of the fibre.

B and B_2, The half-ripe fibre mercerized, and then mordanted with oxychloride of iron, showing the effect of soda in opening the pores to admit the mordant into the body of the wall, and retain it there, as well as to allow of its passing through the wall into the central cavity.

C and C_2, The full-grown cotton mordanted with oxychloride of iron, and dyed in garancine.

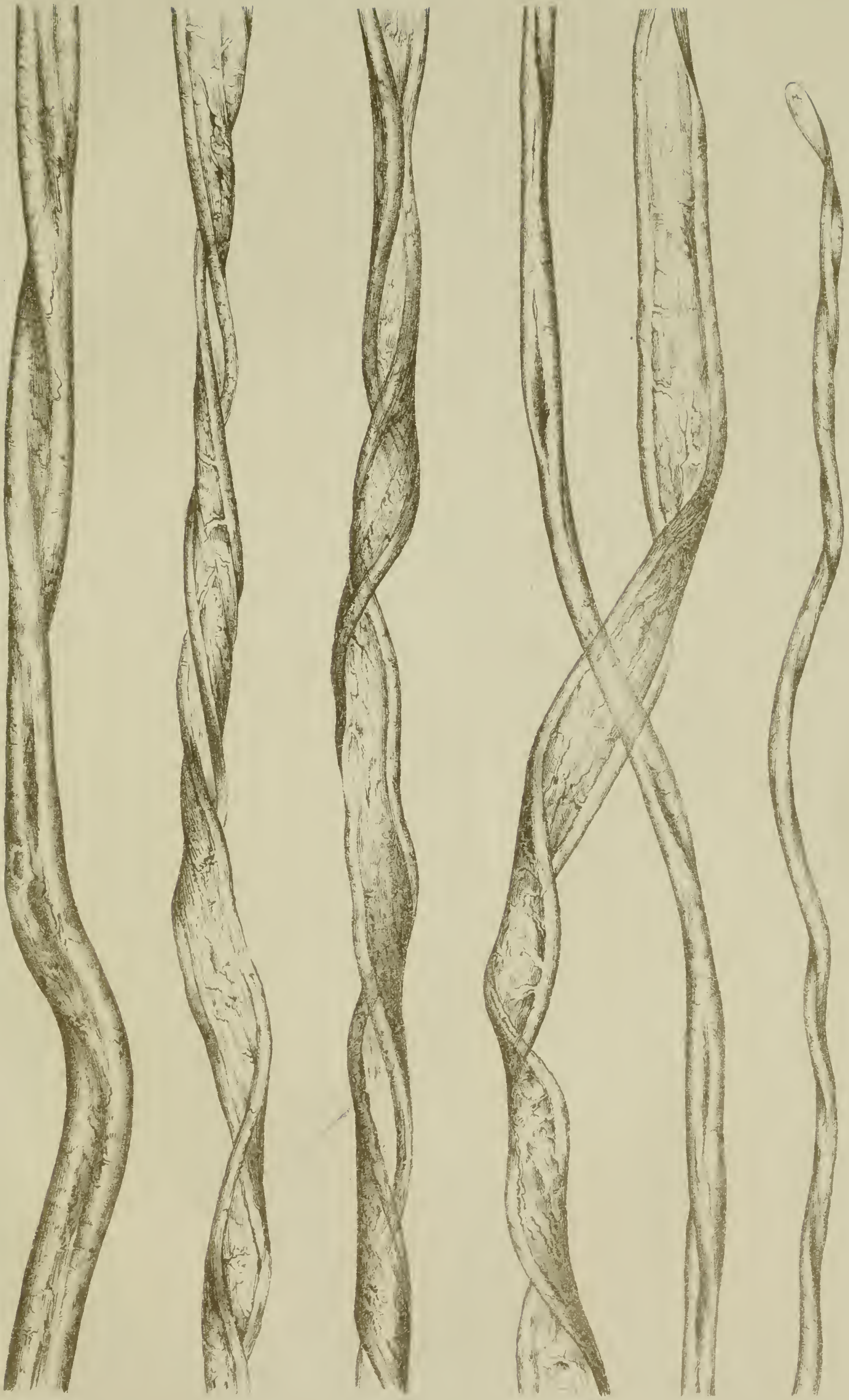
D, Full-grown cotton mordanted with pyrolignate of iron, dyed with madder and soaped. Side views of the same preparation are given at A, Plate IV.

E, The same dye with mercerized cotton. Side views at B, Plate IV.

BELL AND BAIN, PRINTERS, GLASGOW.

PLATE I

MATURE COTTON



E. [illegible] del.

[illegible]

UPLAND COTTON

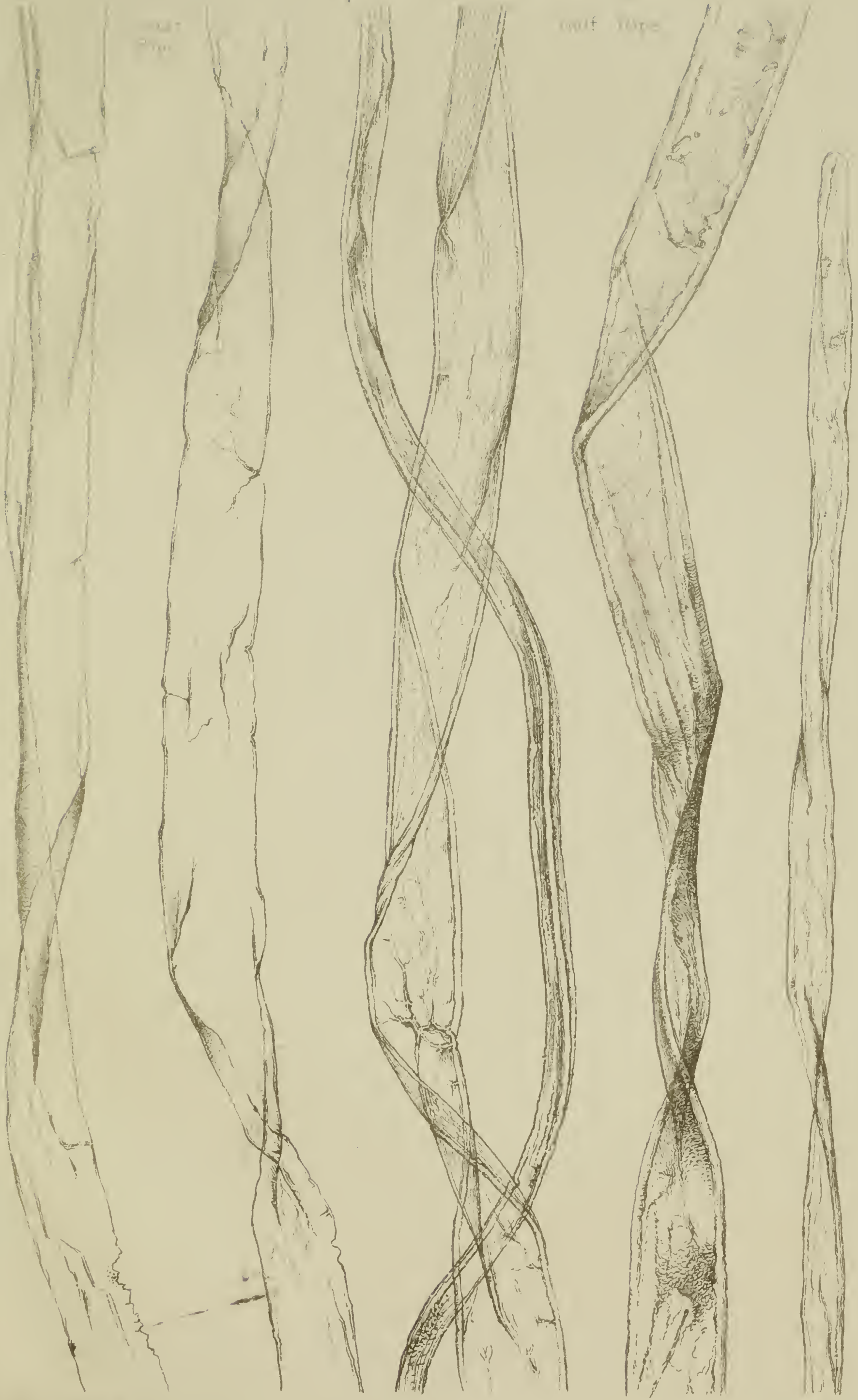


PLATE III

TRANSVERSE SECTIONS OF COTTONS

1. Mature Cotton

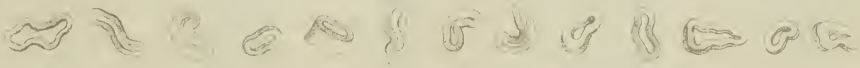
2. Mature Cotton, Mounted Dry

3. Mature Cotton Mercerised

4. Half Ripe Cotton

5. Half Ripe Cotton Mercerised

6. Under 3/4 ths Ripe

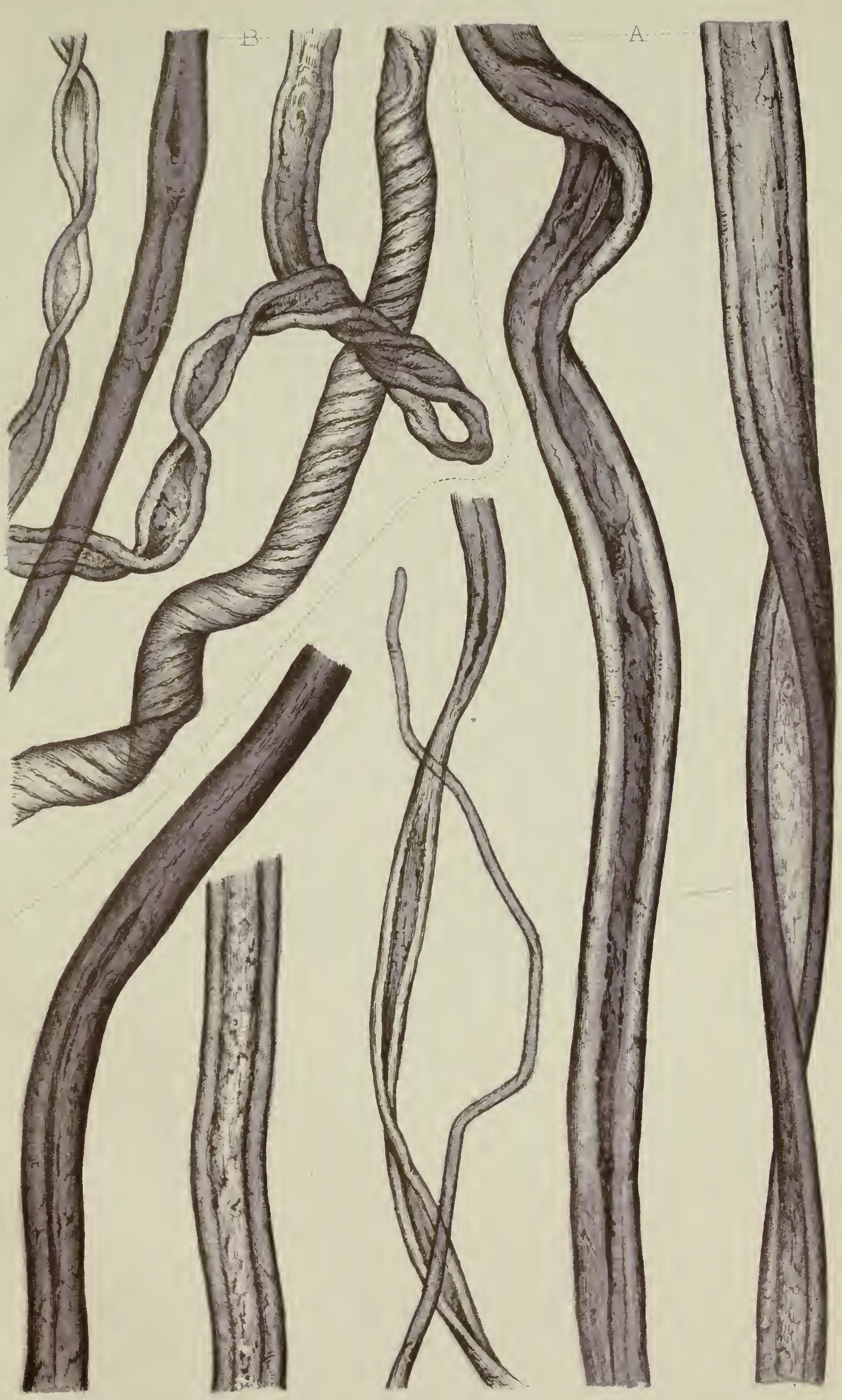


7. Under 3/4 ths Ripe Mercerised

8. The Least Ripe Cotton

Schindler Del.

Parsons & Macdonald Ltd.



E. Schindler Delt

Maclure & Macdonald Lith

COTTON FIBRES WITH THE LAKE OF ALUMINA & MADDER

E. Schaedler Del. [illegible]

PLATE VI

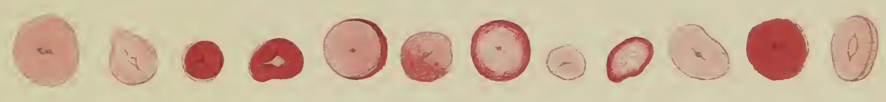
[illegible] SECTIONS WITH THE ALUMINOUS LAKE OF MADDER

1. [illegible] Cotton Mordanted with Acetate of Alumina

2. As No 1 but [illegible] in [illegible] of Madder

3. Mature Cotton Mordanted with Weak Nitrate of Alumina

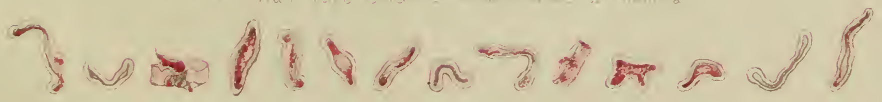
4. Mature Cotton Mordanted [illegible] Acetate of Alumina



5. Mature Cotton Mordanted [illegible] of Alumina

6. [illegible] Cotton [illegible] Acetate of Alumina

7. Half Ripe Cotton [illegible] of Alumina

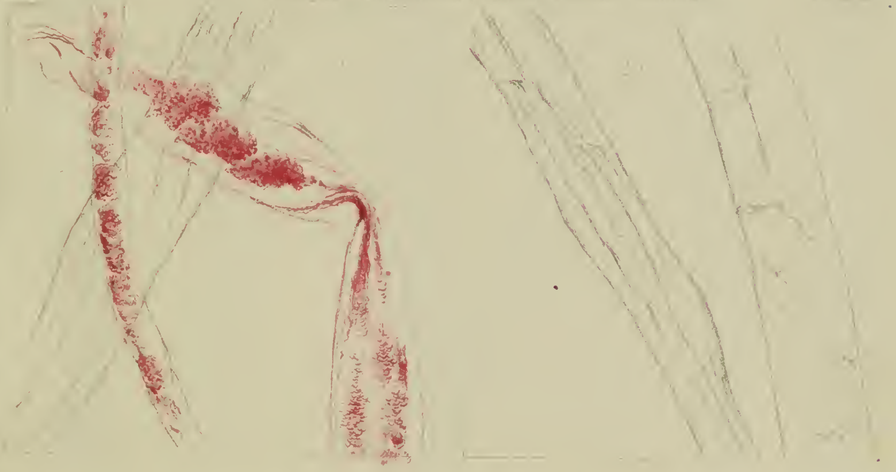


8. [illegible] Cotton Mordanted [illegible] of Alumina

[illegible] Lith. [illegible]

Un-Bleached The Youngest Cotton [illegible] [illegible] [illegible]

[illegible] [illegible] Cotton [illegible] [illegible]



Transverse Sections of Cotton Showing [illegible]

[illegible] del. [illegible] lith.

PLATE VIII

COTTON FIBRES WITH THE LAKE OF IRON AND MADDER

D. Mature Cotton – Pyrolignate of Iron – Madder Dye – Soaped

E. Same as D., but first Mercerised

Schindler Delt

Maclure & Macdonald Ltd