XI IX *On the Manner in which Cotton Unites with Colouring Matter.*

By WALTER CRUM, F.R.S.

THIRD MEMOIR.

AFTER my last communication to the Chemical Society, printed in the January number of this Journal, I intended to do little more on the subject of this paper than to complete the few drawings which were then projected. But being deprived of the assistance in delineating on which I had at first depended, and driven to have the objects drawn under my own eye, it soon appeared that further inquiry would render the investigation much more complete. By then applying myself more seriously than I had before done to microscopic observation, and by taking advantage of the instructions and assistance kindly afforded me by Mr. Hennedy, of Glasgow, in the slicing of transverse sections, together with the valuable co-operation of my assistant, Mr. Walter M'Farlane, in the preparation of materials and dyes, I have been enabled to ascertain the additional facts, and to prepare the drawings, which I now beg to present to the Society.

I shall describe dried cotton, and its behaviour with mordants, in four different stages of its growth :—

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

MATURE COTTON.

Plate I. gives a side view of various forms of cotton fibre in a state of maturity, mounted dry, and magnified about 400 diameters. The shadows are deeper, of course, than when the objects are mounted in fluids, but the inequalities of the surface are also better shown. At No. 2, Plate III., are transverse sections of the same fibre mounted dry; and at No. 1 they appear as mounted in glycerin jelly. It will be observed that few of them have the

complete cylindrical form. I have examined specimens of wool used for spinning, in which that form is scarcely to be found, except at the smaller end. It will be seen, also, from these drawings, that the cotton fibre is not a hollow tube or bag filled with air, and more or less collapsed, as it has hitherto been represented to be, but that in proportion as it is rounded, it has become filled up with apparently solid matter (like the liber fibre of flax), sometimes altogether, and at other times leaving clear passages through the centre.

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 glycerin jelly they appear still more transparent, and in Canada balsam they are scarcely distinguishable from the surrounding medium. At No. 8, Plate III., are tranverse sections of the youngest fibres mounted in glycerin 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 them, 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 glycerin 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 *third 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 fat blade (of dried cotton), whose section shews 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, as well as to physiologists of greater experience who saw the objects, some authority for applying the generally understood principle of a formation of new and separate matter in the process of ripening; and accordingly, in pages 12 and 13 of this volume, I ventured such an explanation. It must now, however, as well as the inferences there drawn from it, be considered unsatisfactory, being without direct evidence, and contradicted—by analogy at least—in so far as it can now be shown 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 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

* The error pervades a great part of pages 12 and 13. It may, in some measure be corrected by substituting the words "*cotton in its expanded form*" where the expressions "*new deposit*" or "*secondary deposit*" occur.

With reference to other statements in pages 12 and 13, it will be observed that colourless openings are now readily seen in the coloured sections, and that new observations have been made on the effect of bleaching on the cotton fibre, and on the growth of cotton in the pod.

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 and 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 recognised 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 pyrolignite 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 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 easily be recognised 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 the e 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 fibres 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 ferrocyanide of potassium. For that purpose a solution of the ferrocyanide 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 redissolves 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 recognised 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 tranverse 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 dialyser.

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 dye^d (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

* 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 be removed from the *1st Class* of dyeing processes, to which I assigned it in my second memoir, page 15, and of which indigo is the type, and placed in the *2nd Class*, as defined at page 5 of that memoir. 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.

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, matt 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, form a solution ($\text{Fe}_2\text{Cl}_3 + \text{Fe}_2\text{O}_3$) 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 garancin, 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 $37\frac{1}{2}$ 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 garancin, which does not require soaping.

The effects are shown in Plate VIII. The unripe fibre, A, acts the part of a membrane or dialyser 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, 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

414 CRUM ON THE MANNER IN WHICH COTTON UNITES, ETC.

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, a quantity of the oxide has been retained in the hollow centre, and but little by the walls themselves.

EXPLANATION OF THE PLATES.

PLATE

- I. Full-grown cotton, magnified about 400 diameters, as seen with Ross's $\frac{1}{8}$ -inch 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 glycerin jelly.
- IV. A, Full-grown cotton prepared with a mordant of pyrolignite 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 and Lealand's $\frac{1}{2}$ -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 garancin. 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 garancin.
 D, Full-grown cotton mordanted with pyrolignite 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.

MATURE COTTON.

UNRIPE COTTON.

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. Cotton $\frac{3}{4}$ ths. Ripe. 7. Cotton $\frac{3}{4}$ ths. Ripe, Mercerised.

8. The Least Ripe Cotton.

COTTON FIBRES WITH THE LAKE OF ALUMINA & Madder.

TRANSVERSE SECTIONS WITH THE ALUMINOUS LAKE OF MADDER.

1. Mature Cotton Mordanted with Acetate of Alumina

2. As N°1, but deficient in quantity of Madder.

3. Mature Cotton Mordanted with Mono Muriate of Alumina.

4. Mature Cotton Mercerised, - Acetate of Alumina

5. Mature Cotton Mercerised, - Mono Muriate of Alumina

6. Cotton $\frac{3}{4}$ ths Ripe, - Acetate of Alumina

7. Half Ripe Cotton, - Mono Muriate of Alumina

8. Half Ripe Cotton Mercerised, - Mono Muriate of Alumina

Un-Bleached The Youngest Cotton with Acetate of Alumina Bleached

Un-Bleached The Youngest Cotton with Mono Muriate Alumina Bleached

Transverse Sections of Cotton, shewing Concentric Rings.

COTTON FIBRES WITH THE LAKE OF IRON AND Madder.

D Mature Cotton - Pyroignite of Iron - Madder Dye - Soaped.

E. Same as D, but first Mercerised.