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I.—*On the manner in which Cotton unites with Colouring Matter.*

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SECOND MEMOIR.

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 mis-statements 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

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

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 general facts.

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 alkalis, 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.

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:—

* 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 cannot discover on what grounds. In my paper on the Nitrates and on Gun-cotton

The combination with soda in Mercerised cotton, if it does exist, is not so stable, and the ultimate constituents of the cotton undergo no change; but, according to Dr. Gladstone, there is a chemical combination $C_{24}H_{20}O_{20}, KO$, which, although decomposable 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 union has ever been supposed to exist between the charcoal and

(Proc. Phil. Soc. of Glasgow, ii, 163, April, 1847.—Phil. Mag., vol, xxx, June, 1847.—Ann. Ch. Pharm., lxi, 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.

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

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

By the use of instruments more perfect than that employed by Mr. Bauer, we find the mature cotton-fibre to be a shrivelled, irregular, partially twisted cylinder, 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 like the tape-worm, to about one-fifth of its greatest diameter, and there its form is more nearly cylindrical and straight.

Under the microscope, the walls of these tubes do not exhibit openings of any kind which can be taken for lateral passages, but it cannot be doubted that like other ligneous matter they are not impervious to fluids. Dr. Carpenter mentions as one of the most remarkable properties of vegetable membrane, its power of allowing fluids to pass slowly through it, even 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 precipitated in its original blue state by oxidation, through exposure to the atmosphere.

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

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 oxidising, 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 and beating 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 colour-

ing (or rather colourable) matter of madder which is itself soluble in water. The practice is, first to apply the iron in solution; and when that is rendered insoluble in the fibre, to give it the opportunity of drawing to itself, through the membrane which contains it, the soluble madder.

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:—

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

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

3rd. That the result of the decomposition,—an insoluble oxide,

—is left there by the volatile acid, which, by its solvent power, had placed it in 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 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. Thom'son, 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 colouring matter. 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 last, I was favoured by Mons. Le Play, 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.

1st. I found that the contents of every capsule which had not

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

opened, and of those which had but slightly opened when 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 same flat, glassy, broad appearance exhibited by the dead cotton fibre already mentioned.

2nd. 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.

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

4th. 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.

5th. 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.

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

7th. 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.

8th. By the kindness of Mr. Henry Cole, I was enabled to examine some dried specimens of New Orleans cotton, also in various stages of maturity, in the South Kensington Museum. The chief difference from the Algerian was that in the American plant the fibre is more mature at the same stage of development of the pod.

I searched for a living plant in the hope of finding the cylindrical fibre filled with sap, as sketched by Mr. Bauer; hoping also to watch the process of thickening of the cell-wall which goes on during the ripening of the fruit, but I could find no fruit-bearing specimen of the plant in any of our public gardens, and nothing has till now been written on the subject. I was kindly furnished by Mr Morris Pollok, of Glasgow, with a cotton-pod from his own garden, nearly full grown, but still green and unripe. Its

fibre did not differ much from the dried unripe specimens from Algeria.

Although the general microscopic appearance of the unripe fibre is that of a single blade, we know from its subsequent history that it is a flattened tube, and therefore double. There is the same indication from the markings upon its surface. These usually consist of short and faint irregular lines—the effect apparently of creases or corrugations of the membrane—which are spread pretty generally over the fibre, and in the direction of its length. At the ends, however, where the fibre has been torn asunder, portions of it may be seen where the membrane is thinner, and the markings fewer than elsewhere; evidently from one side having been torn away from the other. These appearances will be found represented in drawings which are in course of preparation.

This glassy fibre corresponds with the *cellular membrane*, which Professor Henfrey ("Micrographic Dictionary," article VEGETABLE CELL) describes as a primary formation in young plants, and as consisting of a thin structureless pellicle, possessing a considerable degree of toughness, and a certain amount of elasticity, having also no perceptible orifices, and yet readily permeable by water.

During the stay which I made in London in June and July, I was fortunate enough to secure the assistance of Mr. Tuffen West in the renewed microscopic examination I had undertaken of the cotton-fibre, and I take this opportunity of acknowledging my obligations for the valuable suggestions he afforded me in completing the investigation, as well as for his assistance in commencing the drawings which accompany this paper.*

After numerous attempts at obtaining a view of the interior of the mature cotton-fibre, which were attended with only partial success, I procured at last a number of transverse sections, showing tubes of every variety of form, and discovering in the most interesting manner the nature of their contents.

This examination was much facilitated by the employment of dyed as well as undyed specimens of cotton. The fabric from which the most successful of these sections were obtained had been dyed of a red colour, by incorporating it with an aluminous lake of madder. The cotton was first mordanted with alumina by soaking it in a solution of the submuriate of that earth. It was then dyed

* I regret that the illness of Mr. West has prevented me from completing these drawings in time for the present number of this journal

in madder in the usual way, after which it was subjected to the cleansing and brightening which is produced by the action of a hot solution of soap. I was not a little surprised to find the fibre almost entirely filled up with secondary deposit, the internal cavity being reduced to a comparatively small chamber in the centre. Some of the cross sections of these fibres were found under the microscope to be irregular circles, exhibiting the ends of tubes nearly cylindrical. Many of them showed no cavity at all, their whole interior being a mass of red matter, apparently deepening in shade towards the centre. Others were oval-shaped in various proportions of length and breadth, showing generally a small central cavity, circular or long, corresponding to the external outline of the tube. These sections showed also occasionally a fibre hollowed on one side and rounded on the other, with a cavity of corresponding form in the centre. The central openings are sometimes only discernible as dark specks or lines in the centre of the disk, or there appears a dark line surrounding a central cavity of a paler hue. I must add that I have not observed any cavity altogether destitute of colour in a tube otherwise filled with red matter—a fact which must be attributed to the difficulty of forming sections so thin as to allow the opening to be seen in a straight line from end to end, and to the rough spongy character of the deposit which forms the boundary. Diagonal slices frequently occur confirming the apparent character of the disk.

There is a remarkable resemblance between the cavities I have endeavoured to describe and the apertures which appear in the more readily formed cross sections of the liber-fibres of hemp and flax, as these have already been delineated by Mr. Tuffen West, in the "Micrographic Dictionary," and, by the same artist, in a late article on "Cotton," by Dr. Lankester, in the "Popular Science Review."

Longitudinal sections of the dyed cotton-fibre show more perfectly the differences which occur in the amount of colouring matter taken up by the different fibres. These are found in every variety, from the perfectly flat, riband-like, and consequently colourless fibre, like that which is found in the unripe pod, gradually expanding in proportion to the quantity of new deposit which it receives, until it becomes swelled out into the nearly perfect cylinder; and similar differences occur, though to a smaller extent, in the same fibre. Bleached cotton is much more transparent than the unbleached, and takes up in the same circumstances much less dye,

—a large proportion of the secondary deposit having apparently been removed from it by the action of alkalies in the process of bleaching.

From these observations it would appear that the primary cellular membrane, as found in the unripe plant, never acquires the power of absorbing colouring matters; that its only purpose in dyeing is to enclose the soft and granular secondary matter which becomes deposited within it while in progress towards maturity, and that that secondary matter has alone the faculty of attracting those mineral and vegetable substances which are either dyes themselves, or which form dyes by attracting and combining with other bodies. The colourless character of the external membrane, however, is not to be discerned in the well dyed fibre, just as we cannot by mere inspection detect the colourless character of the cell which contains a coloured juice in the natural flower, or like a thin tube of glass which in appearance partakes also of the colour of any fluid that it may contain. It will also be seen from those statements that the deposition of secondary matter within its cell does not commence until after the pod has begun to open, and when it has grown therefore to its full size. These new deposits, says Professor Henfrey, speaking of other plants in which similar substances are formed in quantities sufficient to admit of separate examination, are layers of cellulose, like the primary membrane.

Here, then, are two specimens of cellulose, having the same chemical composition, and subjected to the same process of dyeing, one of them, which is formed by deposition in a manner to expose the greatest amount of surface, and enclose the greatest number of minute cavities, having the power of decomposing certain solutions and entrapping mordants, while the other, a hard, compact, polished membrane, is without appreciable action upon mordants or dyes. The relationship of platinum-black to the hammered metal, and that of wood-charcoal to the diamond, or even to coke, may be taken as analogous, in form as well as in chemical action, to that which subsists between the secondary deposit in the cotton fibre, and the comparatively hard and tough pellicle which encloses it.

These observations seem to me to establish two facts: (1.) That cellulose and oxide of iron do not unite chemically; (2.) That in order to be capable of receiving an iron mordant, the cellulose must be furnished with organs or interstices capable of absorbing

that mordant in a state of solution, and minute enough to hold it when precipitated. Neither the mere matter, therefore, of cellulose, nor cellulose presenting only an open surface, is capable of uniting with an iron mordant.

The almost infinite subdivision in the fibre, of the oxide which forms the purple mordant, may be imagined by considering that the solution of iron which produces it contains often not more than $\frac{1}{8000}$ th of its weight of oxide of iron, and that the cell, therefore, or passage, when filled with that solution, and afterwards dried and changed into sesquioxide cannot (except by one cell robbing another in the act of drying) contain even one-thousandth part of its capacity of the oxide. So minute a proportion of foreign matter cannot be conceived to form an obstruction, even after combination with its colouring matter, to the passage of any solution that may afterwards be applied to the same fabric.

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 chro-

mate 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.

c. Some metallic subsalts give up their excess of oxide in the same manner. Goulard's extract, for example, is almost as suitable for the chrome-orange dye as the plumbite of lime above-mentioned. Sesquichloride of iron, with excess of peroxide, yields but a small portion of its iron to cotton steeped in its cold solution. When heated to near the point at which it becomes turbid, oxide of iron is precipitated abundantly on the cloth, but in a condition no longer capable of attracting a dye. A solution of oxy-chloride of aluminium ($\text{Al}_2\text{Cl}_3, 2 \text{Al}_2\text{O}_3$), of spec. grav. 1.100 deposits a large quantity of alumina on cotton in the cold. It thus forms a mordant for madder and other dyes.

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 oxy-chloride of tin, or still better in a mixture of the bichloride and protochloride, and when, after this preparation with tin, it is immersed in oxy-chloride 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 ferropussic acid, forms a Prussian blue of the greatest richness and brilliancy.

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

B. Acetate of alumina acts in a similar manner.

C. If we wish to fix upon cloth other oxides, such as copper,

manganese, or chromium, which do not spontaneously 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 decomposable, 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; 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.

D. 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.

E. 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 super-additions 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 also apparent in almost all these other dyes; retaining, however, its purity in some more than in others. 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 equally 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.