

XXXIV. Conclusion of Mr. HENRY'S
Considerations relative to the Na-
ture of Wool, Silk, and Cotton, as
Objects of the Art of Dying.

(FROM p. 207.)

FOR the tenth operation, this remaining decoction of galls is to be heated, the thick sediment at the bottom being previously separated by a hair-sieve, and the cotton again treated as in the ninth operation.

The eleventh operation is the aluming of the cotton. Thirty pounds of Roman alum, finely powdered, are put into sixteen gallons of water, gradually heated, and continually stirred; as soon as it becomes so hot that the operator can just easily bear his hand in it, the fire is to be removed. Six gallons of the first barilla liquor are then to be added by degrees, and the whole agitated till the solution is complete. The cotton is to be placed in the wringing-tub, about three gallons of the alum-liquor poured on it, and, in proportion as it is soaked up, more is to be added, till about one half of it is employed. The cotton, having been thoroughly worked in the liquor, is to be well wrung and dried, and the portion which is wrung out is to be returned to the remainder in the pan, and used in the twelfth operation, which is performed exactly in the same manner as the eleventh; after which the dried cotton is to be well washed, by handfuls, in running water, the workman holding in each hand about twenty ounces of cotton, for two minutes. Each portion is then wrung, and separated; washed and wrung again, and laid upon a coarse cloth.

cloth. The whole is then carried up from the river, wrung a third time, and hung to dry. The cotton will now be ready for the thirteenth operation, in which the colouring substance is applied to it.

The cotton is first divided into four equal parts, each of which is to be dyed separately; and these are subdivided into skains, or parcels, of about a pound and quarter each. The copper pan is then to be filled with water, within about six inches of the top, and twenty-six pounds of Smyrna, or rather of Cyprus, madder added to it. As soon as the water becomes milk-warm, fourteen pounds of sheep's blood, as fresh as it can be procured, are to be stirred into it. When the liquor is so warm that the workman can just bear his hand in it, one fourth part of the cotton is to be put into it, suspended on sticks, by means of which it is moved backwards and forwards in the pan, every five minutes; and the skains are to be inverted every ten minutes, so that they may receive the dye equally in every part; this business is continued for about fifty minutes. The cotton is then hung on five sticks

only, and so suspended by strings as to be wholly immersed in the liquor, which is now made to boil, and continued boiling for forty-five or fifty minutes. A white froth, which about this time appears on the surface, is a sign that the madder is exhausted of its colouring matter, and that the cotton can receive no benefit, though it will get no injury, from continuing longer in the liquor. It is then to be withdrawn, carried to be well washed in the river, or wash-wheel, and then wrung and dried.

The other three-fourths of the cotton are then to be successively dyed in the same manner; fresh ingredients being used for each parcel.

The fourteenth operation is represented as highly essential to the success of the process; should it be omitted, the colour, it is said, would not only be so unfixed as to lose much in the subsequent operation, but would likewise require more time for the enlivening. About eight gallons of the white liquor, which remained after the seventh operation, and were directed to be reserved, are now to be mixed with four gallons of the first barilla ley. Two gallons of this mixture

mixture being put into the wringing-tub, the whole of the cotton is to be washed in it; adding more liquor in proportion as it is soaked up by the cotton, which is afterwards to be wrung and dried.

To this succeeds the fifteenth and last operation; viz. that of enlivening or reviving the colour. The copper pan being about half filled with water, twenty-eight or thirty gallons of the liquor remaining after the first operation are to be added, so that the liquor may reach to within six inches of the top. When the liquor is nearly boiling, the cotton is to be put in, being previously formed into parcels of about two pounds and a half each; nearly four ounces being kept separate, for a purpose hereafter to be described.

The cotton is to be well pressed down in the pan, and confined by sticks. The pan is covered with a wooden lid, having a small hole, through which the small portion of cotton, reserved for that intention, may be occasionally withdrawn, in order to observe the progress of the operation; this hole has a movable cover. The lid is then to be secured by a strong cross of wood, with a straight piece over it; and the sides made close,
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so as to confine the vapour, by laying round the edges of the lid a quantity of damp linen cloth. The fire is then to be raised, so as to make the liquor boil, and the boiling is to be continued for nine hours.

The process is finished by taking the cotton out of the liquor, wringing, and drying it; but the drying is never to be performed either in a stove or in strong sun-shine. The colour will be most brilliant if the cotton be dried in the shade, with a free access of air.

In the third part I shall endeavour to give a theory of dying, (as far as *bases* are concerned,) and especially of the process of which we have just given a detail.

P A R T T H I R D.

Nothing can lead more effectually to the improvement of any art than a right understanding of the instruments, or agents, employed in the practice of it. Though long experience may establish a number of facts, yet, if the *rationale* of the manner by which they are produced be not understood, misapplications are liable to be made;
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similar practices are pursued where the cases differ essentially; and improvements are attempted at hazard, and often on false principles.

Though it may not be granted that, in the scouring of the several materials which are to be subjected to the art of the dyer, their tubular pores are enlarged, or even divested of any matter which obstructs them, yet it will not be disputed that the intention of these processes is to remove an oily or a resinous matter which invests the fibres, and fills up the interstices of the filaments; either rendering the material less white, or lessening its attraction for water, and for the colouring matter intended to be applied. For the more brilliant colours, in order that they may be exhibited in their greatest lustre, the scouring and bleaching is generally carried to such a degree as only to be short of injuring the texture; and the material always suffers a loss of substance.

In the preparation for the Turkey red, the case seems to be different; no bleaching is allowed, and the first operation of the process is of a kind that is rather likely to add to the weight than to subtract any thing from it. The cotton is boiled
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in a mixture of barilla, or impure mineral alkali, oil, and animal excrement. Were the sole intention of this operation to scour the cotton, or, as the dyers phrase it, to open its pores, would not the barilla alone be more efficacious? And for what reason can we suppose that the sheep's dung, which contains a quantity of foul colouring matter, should be added? We have seen that, in the scouring of silk, where a perfect soap is used, some portion of it adheres, notwithstanding the washing the silk undergoes. The cotton is indeed also well washed after this first operation, but it is most likely that water will not be able to remove the whole substance of this animalized soap; and it seems also probable, that the imperfect soap, or mixture of oil and alkali, together with the dung-liquor, through which the cotton is so often passed, will continue to furnish somewhat to it; for, animal substances contain an acid which is separated in various forms. We have already seen that saccharine acid is obtainable from them by means of nitrous acid; the blood affords the Prussian acid, and also phosphoric acid. This last is contained still more abundantly

abundantly in the urine, and in the bones, but we shall defer the consideration of the use of animal acid in dying, till we come to treat on the subject of bafes.

The idea of animalizing vegetable substances, to promote their attraction for colouring matter, occurred to me many years since; and the late Sir Torbern Bergman seems to have held a similar opinion. We have seen, in the abstract I have given of M. Berthollet's analysis of animal and vegetable substances, that wool and filk yield much acid of sugar, together with a fatty oil; whereas cotton gives no saccharine acid, no oil, and, in short, that the whole substance is capable of being dissipated in the form of gas, leaving no residuum in the retort, and communicating nothing permanent to the nitrous acid which distils into the receiver.

I wish that some person, whose opportunities and leisure are greater than mine, would compare, by such an analysis, cotton in its natural state, and cotton prepared in the seven leading operations for the Turkey red; in order to determine whether it have, by this treatment, acquired pro-

perties more nearly approaching to animal matter; viz. whether in the latter state it will afford more acid of fugar, and give over on distillation an oily matter, resembling that obtained from animal substances.

Another point which it might be important to ascertain is, what increase of weight the cotton acquires after each steeping. It appears from the account of the gentlemen appointed to superintend and repeat M. Borelle's process, that, previous to the maddering, or imparting of the colouring matter, the cotton had increased to the amount of $\frac{2}{3}$ of its original weight, though it had been well washed previous to that operation. In this increase, however, was included what it had acquired in the operations of galling and aluming.

The operation of galling, in this as well as some other processes of dyeing, is used previous to the application of the basis to the material. Galls contain an astringent matter, to which chemists have lately given the appellation of the astringent principle, and the Dijon Academicians have proved it to be of an acid nature. It has not only the property of decomposing metallic, but also earthy,

earthy, solutions, and of combining with the precipitates which fall from them: hence its use, previous to the aluming, in the process of dying. Steep cotton which has not been galled in a solution of alum, the solution will remain clear, and the cotton, when dried, will be covered with aluminous crystals: let another parcel of cotton, which has been galled, be immersed in a similar solution, the liquor will become turbid, and plain marks of precipitation will appear.

This astringent principle is of still farther use in the art of dying, and we shall presently see the manner in which it acts, when combined in those vegetables which afford colouring matter.

Having thus given an account of the previous operations in dying, relative to the application of the basis, let us next enquire into the principles on which this application is made, and the modes by which it is more firmly attached to the material.

We have already remarked that alum contains an earth in its composition, united to vitriolic acid. This earth is purely argillaceous, and may be separated from the acid to which it is united, by any substance to which either the earth,

or the acid, has a stronger attraction than they possess to each other.

The first theory we meet with, to account for the action of alum, and other intermediate substances used to furnish bases for colouring matter in dying, is that of M. Hellot; who supposes that these saline bodies form vitriolated tartar, a salt difficult of solution in water, and that the minute crystals of this salt insinuate themselves into the pores of the material to be dyed; that to these crystals the colouring matter becomes attached, and firmly united, and they to the material, so as to resist the solvent power of water. Thus, when tartar and alum are used, he imagines the vitriolated tartar to be formed from them; and, in every other case of dying, he accounts for the production of a vitriolated tartar, but often in a manner by no means satisfactory. This vitriolated tartar he describes as crystallizing in the dilated pores of the cloth, attracting the colouring matter, and, being difficult of solution in water, detaining the colouring particles, which are farther cemented by the crude tartar.

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But, though these salts are not *easily* soluble in water, yet a *sufficient* quantity of water will dissolve them; and, if the colouring particles were attached to them, they must be carried off whenever the solution of the salts is effected. But, as this is not the case, (for, when these particles are properly affixed to the material, they are not movable by any quantity of water, however large,) their fixity must depend on some more permanent basis.

Mr. Keir, the ingenious translator of Macquer's Dictionary of Chemistry, appears to have been the first who suspected that the earth of alum was precipitated, and in this form attached to the material; indeed, it seems wonderful that this idea did not occur to M. Hellot, who was fully aware that, in the dying of scarlet, the cochineal became firmly united to the white calx of tin.

M. Macquer, in the last edition of his Dictionary, has been more explicit on this subject. From the experiments which have been alluded to, in the second part of this paper, by which laques and carmine are made by pouring solutions of alum, or of tin, into clear decoctions of extractive
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refinous colouring ingredients, he concludes that the same effects take place in dying; that, when the materials are loaded with these earthy or metallic salts, and then thrown into the liquors impregnated with the colouring substances, the colouring matter quits the other principles to which it was united, seizes on the earthy basis of the salt, and, uniting with it, loses its solubility in water; and, in this combination, becomes attached to the material, in so permanent a manner as not to be washed away by water. M. Macquer, however, does not seem to have been aware, that it is by means of the astringent principle that this precipitation is effected. All the substances which form laques contain this principle; as is evinced by the blackness they produce with martial solutions, and to this the colouring principle seems to be closely united. A few drops of infusion of galls produce an immediate precipitation of the earth of alum from its acid: this precipitation is more copious than that produced by any of the common colouring substances, and is, at the same time, white.

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Here again new experiments are suggested. Let a large quantity of earth of alum be thus precipitated by galls; let the precipitate be well washed, and afterwards exposed in a retort, with a receiver adapted to it, to a strong heat; the astringent principle, if united to the earth of alum, being volatile, will probably be driven over into the receiver, and thus the supposed combination be rendered evident.

Again, let the supernatant liquor, from which all the earth has been precipitated, be examined, to see in what state of combination the vitriolic acid of the alum remains.

In the common dyes then, with metallic or earthy bases, the theory is pretty clearly as M. Macquer has represented, only taking the astringent principle into the account; and, with respect to wool and silk, nothing more seems necessary than the impregnation of the one with alum and tartar, and of the other with alum alone, previous to their immersion in the coloured liquor.

But when cotton is to be dyed, and some of these bases are requisite, not only the basis is to be precipitated by the astringent colouring principle,

ciple, but the attraction of the material to the basis is to be increased by other *intermedia*. The permanency of the extractive dyes, therefore, depends on the previous treatment of the cotton; and, where alum is employed, of that salt, so as to procure a more copious precipitation of its earth, and to unite it, by means of other substances, to the material.

For this reason, in the common dyeing of cotton the alum is previously neutralized, by the addition of alkaline salt; whereby, not only the acid is prevented from injuring the cotton, but the alum is put into a state more ready to be precipitated by the astringent colouring matter.

For this reason also, in the process of calico-printing, the earth of alum is made to change its natural acid for the acetous; for, by this means, not only a salt is prepared, capable of dissolving more copiously in water than common alum, but the acetous acid, being more loosely attached to the aluminous earth, is, as it becomes concentrated by drying, easily driven off by heat, the earth being left spread upon, and cemented to, the calico.

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When speaking of the use of animal substances, it was observed, that they yield several different acids by various modes of analysis; viz. the phosphoric, the sebaceous, the Prussian, and the saccharine. Of these, the two first are formed in the animal system; the third is perhaps the creature of fire, and originates from a combination of some of the more simple constituent parts of animal substances; and, of the last, it should seem that these substances only contain the basis*. M. Berthollet, by uniting caustic alkalies with animal substances, is said to have found them neutralized, and that the animal matter, when afterwards separated from the alkali, is no longer susceptible of putrefaction. This animalized neutral salt may be decomposed by means of alum; and, while the vitriolic acid seizes on the alkali, the earth of alum becomes intimately combined with the animal acid. It appears to me highly probable, that this acid is supplied to the cotton, in the process for dying the Adrianople red; that the attraction between the cotton and acid being strong, and that between the latter and the earth of alum being likewise

* Critical Review, vol. LXII. p. 377.

powerful, such an union is effected as assists in rendering the material capable of attracting and retaining the colouring matter, in as forcible and permanent a manner as can be done either by wool or silk.

The use of the galls also, in this and other processes, seems intended to promote a similar purpose. Cotton, either unbleached, or which has undergone no process but that of bleaching, when immersed in a solution of alum, produces no change in the appearance of the solution; but, as has been already shewn, cotton previously steeped in an infusion or decoction of galls soon renders the liquor turbid, occasioning a precipitation of the earth of alum on the cotton.

The imperfect soap also, formed by the union of the alkali and oil, when mixed with the alum, will both decompose that salt, and be itself decomposed, and a soap of a different nature will result, from the union of the oil with the earth of alum. M. Berthollet, who has made several experiments on earthy and metallic soaps, found this argillaceous soap to be totally insoluble in water, and in spirit of wine. It is probable also, that the blood, which is employed with the mad-
der,

der, may supply both animal salts, and a glutinous matter, to the cotton. This seems to be the use of the blood, and not, as M. Borelle supposes, to communicate a pink tinge to the madder.

Here then appear to be several different substances employed, tending to form insoluble compounds with the argillaceous earth of the alum. But whether, when deposited on the cloth, they remain so many distinct compounds, or may all unite into one insoluble body, I do not pretend to determine.

M. Macquer, whose opinions always deserve the most respectful attention, declares, that the excellence and permanency of the Turkey red depend on the great quantity of alkali, used in the process of aluming, redissolving the earth of alum, after its separation from the vitriolic acid, and forming with it a saline compound, easily separable into its constituent parts, so that the aluminous earth may be conveniently deposited on the cotton, and united to the colouring matter. The following is a translation of his own words, from the last edition of his Dictionary.

“ In examining,” says this excellent chemist, “ the effects of all the complicated operations at-

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“ tendant on the Levant, or Adrianople, process,
 “ for giving to cotton a more beautiful and
 “ durable red, by means of madder, than can be
 “ communicated by the common method, I
 “ was struck with a singularity which attends the
 “ aluming in this process, and which consists in
 “ mixing a great quantity of fixed alkali with the
 “ solution of alum, previous to the impregnation
 “ of the cotton with it.

“ As the alum is certainly decomposed by the
 “ fixed alkali in this operation, I wished to dis-
 “ cover what was the result; and I found that
 “ the alkali, at the instant it precipitated the
 “ earth of alum, redissolved a considerable part
 “ of it, and that the alkaline salt, with aluminous
 “ basis, is the real mordant in the Levant process.
 “ I have actually determined, by suitable experi-
 “ ments, first, that both fixed and volatile alkalies,
 “ especially if caustic, are capable of dissolving and
 “ reducing to a saline state a sufficiently large por-
 “ tion of earth of alum, even in the moist way; and
 “ that, by calcination, fixed alkalies become ca-
 “ pable of dissolving a somewhat larger quantity of
 “ this earth; secondly, that this alkaline earthy
 “ salt is decomposed, even by water alone, but still
 “ more

“ more easily by means of a decoction of madder,
 “ or other extractive tinctures, on the colour of
 “ which the earthy part of the salt seizes, and
 “ forms with it a laque, or coloured precipitate, in
 “ the same manner as those mordants which are
 “ formed of an acid combined with an earth or a
 “ metal; thirdly, I have proved, by several
 “ experiments, that when cotton or linen is im-
 “ pregnated with a strong solution of this alka-
 “ line mordant, without any other preparation
 “ than scouring and galling, these substances re-
 “ ceive, in the madder-bath, a red much more
 “ beautiful and deep than can be given them,
 “ when alum alone is used *.”

Notwithstanding my deference for the opinion
 of this great man, I must, on this occasion,
 differ from him, for reasons which, it is hoped,
 will prove satisfactory.

1st. The portion of barilla used in the operation
 of aluming is only six pounds, supposing the whole
 quantity employed to be dissolved in the first li-
 quor; but, as there are two other solutions made

* Macquer, Dictionnaire de Chymie, 2 edit. tom. 4. Article
 Teinture.

before

before the whole of the salt is dissolved, it is probable that six gallons of the first liquor will not contain near one half of that weight; for, the barilla being dry and hard, and the mineral alkali less soluble than the vegetable, the first water will act but slowly on it; and it is observable, that, through the whole process, the second liquor is considered as the strongest, and is used for mixing with the oil. Besides, not much above one half of the barilla consists of aerated mineral alkali; we may therefore conclude, that the amount of this salt contained in six gallons of the first barilla liquor (the quantity added to thirty pounds of alum) does not exceed one pound and a half. Now, as 100 parts of alum contain 38 of vitriolic acid, these will require, for their saturation, 37 of aerated mineral alkali; so 30 parts of alum, containing 11.4 of that acid, these will require, for their saturation, 11.1 of the same alkali; whereas, the quantity employed amounts only to 1.5, or rather more than $\frac{1}{3}$ of the quantity requisite for the neutralization of the acid; and, as a superabundant quantity of the precipitant, above what is necessary to the saturation of the acid, is requisite before re-solution of the precipitate

precipitate can take place, we have, in this case, no reason to expect it.

2dly. The quantity of alkali employed is not superior to that used in the aluming, in other processes for dying with madder; viz. $\frac{1}{6}$ or $\frac{1}{8}$ of the alum.

3dly. The alkali, being aerated, is in the most unfavourable state for redissolving the aluminous earth; and,

4thly. The re-solution of the aluminous earth takes place only so long as any of the superabundant vitriolic acid remains unneutralized, except the addition of alkali be continued after the precipitation of the aluminous earth is wholly effected; and it cannot be supposed that the alkali, with which the cotton has been impregnated, in the previous operations, added to that contained in the barilla liquor, mixed with the alum, can be such, even if it were in an uncombined state, as to produce supersaturation.

It should seem probable, therefore, that the permanency of the Turkey red depends on the causes already assigned, and that its brightness is produced by the action of the mineral alkali on the madder. This appears, at first sight, discordant

cordant with the theory of Mr. Delaval, that alkalies reduced red colours to crimson, and these to purple; whereas, in the present case, the red is brightened by boiling in a strong solution of mineral alkali; but the fact is perfectly agreeable with that theory; for, the madder-colour is too much inclining to a dusky orange, and this, by means of the incrustating alkali, descends to red.

Before I conclude, permit me to advance a few circumstances relative to the black dye.

For the dying of black, the calx of iron is the mordant employed, and this, uniting with the astringent principle of the galls, forms a black pigment, which is attracted by, and adheres to, the material to be dyed.

The late Dr. Lewis had ascertained, by a number of well-conducted experiments, that the colouring matter of ink consisted of a very finely attenuated calx of iron, combined with this principle. He found also, that this matter, (which, if not kept suspended by some mucilaginous substance, separates and precipitates from the liquor,) resembles in some degree martial æthiops; but that it was not, like that powder, attracted by the magnet till after it had been exposed to a red

heat, when it lost its blackness, and became of a rusty brown colour; a proof that the black colour of ink, or that of the black dye, which is formed on similar principles, does not depend merely on the iron acquiring phlogiston from the galls. He also found, that both acids and alkalis destroy blackness thus produced; the former by dissolving the ferruginous body, the latter by acting on the astringent principle; he, however, was of opinion, that this principle was of a fixed, not of a volatile nature. But our worthy president, Dr. Percival, very early suspected that this astringent principle possessed some volatility; in support of his opinion, he mentions artichoke-stalks losing their astringent principle by being dried in an oven. He likewise appears to be the first who observed the action of acids and astringents on each other.

The subject has been farther pursued by the Dijon Academicians; from the result of whose experiments it appears, that the astringent principle is soluble in water, in spirit of wine, in oils, and in ether; that it rises copiously in distillation, reddening the blue vegetable juices, but is capable of uniting, with equal facility, with acids

and with alkalies; that, though it does not revive iron, without the aid of fire, yet gold and silver are precipitated by it in their metallic form; and that it is capable of decomposing most metallic solutions; and of giving different colours to their precipitates.

Dr. Percival had endeavoured to produce an ink, by macerating iron filings, without their being combined with any acid; but, making his infusion without heat, he did not succeed. The Dijon chemists, not content with making a similar attempt, boiled the liquor; and thus obtained a violet-coloured ink, the traces of which were as well defined, and permanent, as those produced by ink prepared in the common way, even without the addition of gum. Hence it should seem, that the heat not only enabled the astringent principle to dissolve the iron, but also extracted a mucilaginous matter, which supplied the place of gum.

I have related these facts, in order to elucidate some circumstances attending the dying of black. Green vitriol was formerly used, but the calx of iron is too much dephlogisticated in this salt, and the black produced by it is not permanent. Solutions of iron in acetous acid have of late been
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preferred, especially for cotton; and even solutions of that metal, made by macerating it with alder-bark and water, in which the astringent principle should seem to unite with the vegetable acid to form the solvent. In these solutions the iron is not too much deprived of its phlogiston, and, contrary to those made in mineral acids, they improve with age; for, the vegetable acid tending to putridity evolves phlogiston, which unites with the iron; whereas the vitriolic solution is continually parting with that volatile principle, and thereby not only becoming less fit for producing blackness, but the calx of iron, when highly dephlogisticated, is very injurious to the texture of the cloth.

The improvements made in dying black are perhaps the strongest proofs that can be given of the utility of chemical knowledge; nor can a more apt instance be adduced of the inconvenience arising from the want of it than the French process, related by M. Macquer, for this purpose; in which no less than thirty different ingredients are directed to be employed, several of which are the same things under different denominations, and others tend directly to destroy each other.