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A MONTHLY

JOURNAL OF BLEACHING, PRINTING, DYEING,

AND

FINISHING TEXTILE FABRICS,

AND THE

Manufacture and Application of Colouring Matters.

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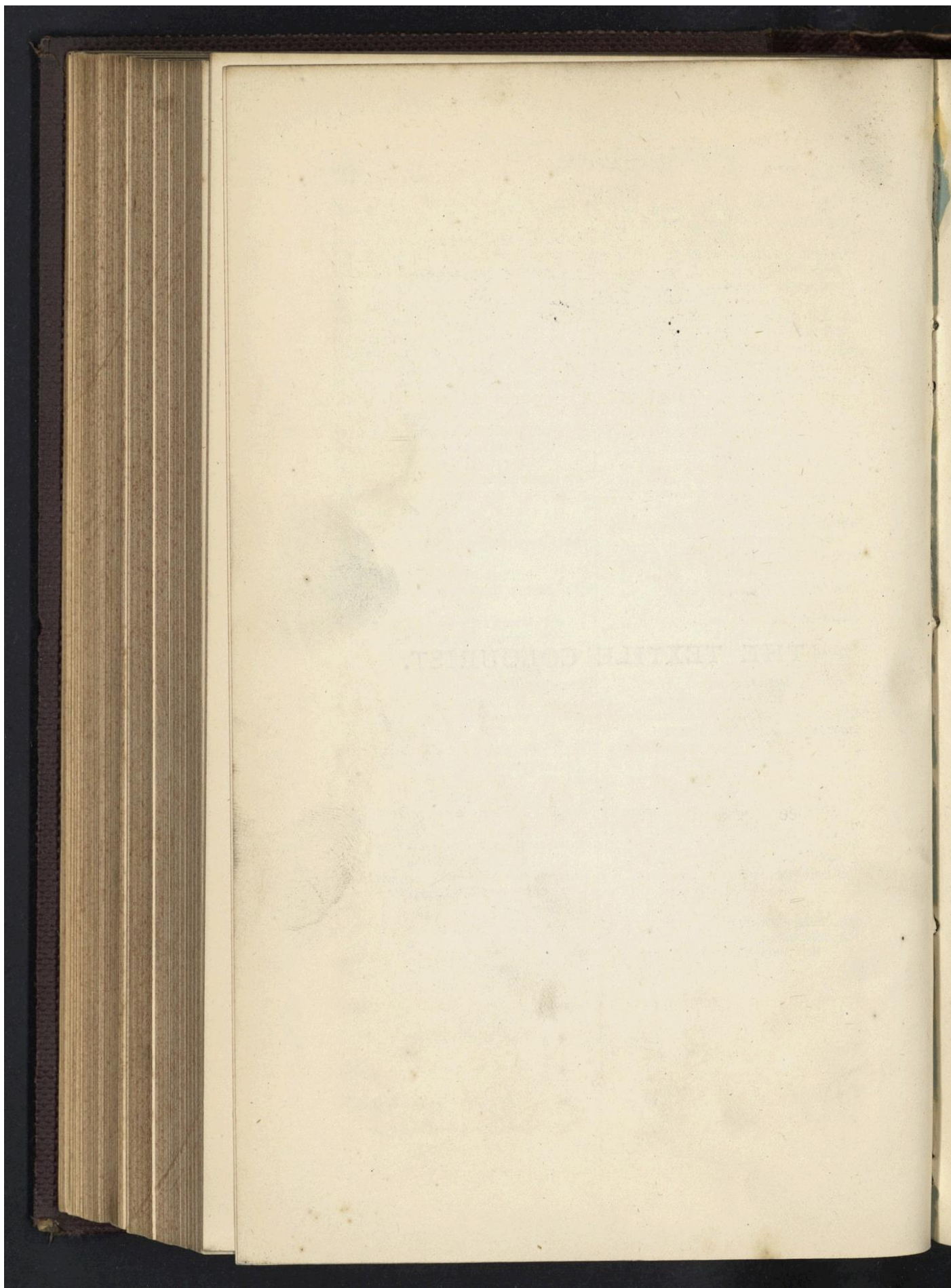
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[Vol. II.]

1. Colours from Naphthylamine upon Cotton.

[We extract the following particulars upon the naphthylamine colours from an excellent study upon the subject, by M. F. Rhem, which has been published in the Bulletin of the Industrial Society of Rouen.*]

THE method at present employed for obtaining these colours is founded upon the process of Roussin, and consists in placing in a cast-iron vessel 6 parts of hydrochloric acid and 1 part of nitronaphthaline, and then adding as much granulated tin as is required to make it appear above the surface of the liquid mixture; the vessel not being more than half full is heated in a water bath, and the nitronaphthaline speedily disappears. The liquid is now drawn off and mixed with half its volume of water; when the whole becomes nearly solid, owing to the crystallization of the hydrochlorate of naphthylamine, the crystals are pressed, redissolved in boiling water, and the tin which is in solution removed by the addition of a suitable quantity of sulphuret of sodium. The precipitate carries down with it a quantity of tarry matter. After filtration the solution is left to crystallize, and yields tolerably pure crystals of the hydrochlorate which are pressed and dried. This salt distilled with caustic lime yields the base naphthylamine, which appears in white needle-like crystals of a silky touch; it soon becomes coloured when exposed to the air, acquiring a purplish or rather wine-red hue. It has a powerfully disagreeable odour

* Vol. iv., p. 29.

which is very persistent. It melts at 122° F. and boils at about 570° , distilling without decomposition. It is nearly insoluble in water, but very soluble in alcohol, ether, and aniline. Kept from the air and light it remains permanent and unchanged for years. When acted upon by oxidizing agents, such as perchloride of iron, nitrate of silver, the chlorides of gold and platinum, or the bichloride of mercury, this base and its salts give a blue substance called naphthameine. Heated with nitrate of mercury, or chloride of tin, it yields red colours.

For a long time past it has been sought to employ the naphthylamine colours in dyeing and printing, but the results have either been negative or not sufficiently promising. A great difficulty in this matter is its powerful and disagreeable smell, which infects the hand and clothes of those who work upon it with such persistence that much washing and a considerable time is required to get rid of it.

The colours which have been obtained up to the present time have been deficient in depth and brightness, but there are some of them which have been applied with tolerable success. They are neutral shades, greys of an agreeable tone and perfectly even in hue. Their chief value is in their fastness and resistance; neither acids, alkalies, air, nor light, cause any appreciable change in them. Acted upon strongly by chlorine they are reduced, and acquire a more yellow tone. They are the fastest colours known, and from this merit alone they will sooner or later find their proper place and employment by those manufacturers who are not afraid of a bad smell in their operations, for it appears that this defect is less observed when working upon the large scale than in small trials.

The method of application is easy and cheap, and the colours can be easily combined, and submit to the methods necessary in certain classes of colours, such as aniline blacks, chrome orange, iron buffs, indigo blues, steam blues, and in general with all steam colours.

The naphthylamine colours can be obtained by steaming, especially the lighter shades, and also by fixing in soda, lime, and chrome, just as may be required by associated colours; the shades certainly change by different treatments, but they

are always delicate and pleasant. The common dunging operation for madder colours gives very good results with these colours.

An inconvenience attending these colours in printing is that of obtaining a good white with dark shades; the doctor does not completely clean the colour from the roller, and the trace which is communicated to the cloth, developes and fixes beyond the clearing power of chlorine or soap.

Naphthylamine is preferably applied with the muriate of iron, as the shades are brighter and more regular than with any other mixture, but this colour does not keep well, and there is some irregularity from this cause. The naphthylamine can be advantageously mixed with different quantities of aniline salt, or with aniline grey or black, the yellowest shades can by this mixture be modified into all hues of grey.

The ageing of naphthylamine colours requires great care, and is best accomplished by first giving a few hours in a warm and quite dry place, and afterwards one or two days in an ordinary ageing room.

The following formulæ were employed by M. Rhem, in making colours for printing :—

Fancy Shade. Yellowish.

- 1 gallon water.
- 1 $\frac{1}{4}$ lb. starch.
- $\frac{1}{2}$ lb. naphthylamine.
- 2 $\frac{1}{2}$ oz. chlorate of potash.
- 1 $\frac{1}{2}$ oz. salammoniac.
- $\frac{1}{2}$ lb. acetic acid.
- 2 oz. hydrochloric acid.
- $\frac{1}{4}$ lb. protomuriate of iron, at 75° Tw.

Reduce for paler shades with starch paste.

A greyer shade can be obtained from the same composition by substituting nitric acid for the hydrochloric.

Naphthylamine Grey.

- 3 parts of the above colour,
- 1 „ starch paste.
- 1 „ aniline grey.

Starch Paste.

1 gallon of water.
1 $\frac{1}{4}$ lb. starch.
 $\frac{1}{2}$ lb. acetic acid.
1 $\frac{1}{2}$ oz. olive oil.

Aniline Grey.

1 $\frac{1}{2}$ gallon tragacanth gum water.
6 oz. salammoniac.
6 oz. chlorate of potash.
 $\frac{3}{4}$ oz. muriate of aniline.
5 oz. nitrate of copper at 84°.
6 oz. hydrochloric acid.

M. F. Rhem has added three illustrations of colours printed upon calico according to the above receipts. We are afraid it may be said that the shades have nothing but their fastness to recommend them, the colours are not full or saturated, neither soft nor bright, and the whites as M. Rhem led us to anticipate are very inferior. Small patches pasted in books seldom do justice to the colours shewn, and it is hardly fair to draw conclusions from them, but in this paper it is admitted that the experiments are only at the beginning. Attention may be here drawn to the following paper which is upon the same body.

2. *Chocolate Colours from Naphthylamine.*

THIS paper is abstracted from a lengthy communication of M. F. Lamy to the Industrial Society of Mulhouse, which is inserted in the same Bulletin as the last paper. The results obtained by M. Lamy, as illustrated by the printed specimens inserted in the original, are of a much higher character than those shewn by M. Rhem. The chocolate in one of the patches is pure, rich, and deep, and the white perfect; in the other samples where the chocolate is printed in combination

with chrome orange in one case and aniline black in the other, it does not appear quite so rich as in the single-coloured illustration, but still is so good as to lead to the hope that something valuable to the calico printer will yet come out of naphthylamine. We give those parts of M. Lamy's paper which have the most interest.

After stating that he had made some use of the naphthylamine colours for the last few years, there was one upon which he particularly directed his attention, and which was worked by him in 1869 at Besselièvres, it is the brown or chocolate colour.

While repeating the experiments upon the action of oxidizing agents upon naphthylamine and its salts, he observed that when a hot and strong solution of salt of naphthylamine was mixed with a concentrated solution of bichromate of potash containing hydrofluosilicic acid, a strong effervescence was produced and a dark brown precipitate formed, which, when treated with ammonia or chloride of soda gave a pretty lively chestnut colour, which, however, lost its brightness by drying. The method of the preparation was as follows :—

In 3 decilitres of water dissolve
50 grammes hydrochlorate of naphthylamine,
Then add by little and little the following mixture :—
1 decilitre of boiling water.
50 grammes bichromate of potash.
50 grammes hydrofluosilicic acid at 20° B.

The precipitate formed is insoluble in water, nitric acid, ammonia, and alcohol ; it is slightly soluble in acetic acid.

It was then attempted to produce this brown precipitate directly upon cloth, and M. Lamy eventually succeeded. In fact, if calico be steeped in an alcoholic solution of naphthylamine, dried, and then passed into a mixture of bichromate and hydrofluosilicic acid, the brown colour is at once fixed upon the cloth; if it be then washed in a calcareous water a shade of brown, varying in intensity with the concentration of the naphthylamine solution, is obtained. In this state it is deficient in brilliancy. By submitting it to the action of ammonia and chloride of soda it is brought to a chocolate

shade of some brightness, but which communicates a rough, unpleasant touch to the cloth.

If the salts, and not pure naphthylamine be employed, as for example the hydrochlorate or the nitrate, the result is much better. Chocolate and puce shades are obtained tolerably bright, and resembling a garancine chocolate, dyed with addition of yellow wood. From this experiment to the application by printing was only a step.

By thickening a sufficiently strong solution of salt of naphthylamine with starch, adding chlorate of potash, passing in bichromate and acid, and lastly in chloride of soda, the colour is obtained. Another method consists in passing the cloth into a hot and strong chrome liquor, but it was found not practicable on the large scale on account of the liquor becoming too dirty, and the colour did not possess the same brightness as that obtained by passing in bichromate and acid in the cold.

The most suitable thickenings are starch and tragacanth; the gum thickenings give only a reduced Havana or cigar shade. The hydrochlorate of naphthylamine does not give so good a colour as the preparation about to be described, which is, in fact, a solution of the nitrate of naphthylamine in acetic acid. The hydrochlorate is also more difficult to print, on account of its sparing solubility in the cold, it soon crystallizes, sticks in the engraving, and spoils the whites.

The naphthylamine should be as pure as possible, if it contains naphthaline it gives dull colours; some specimens contain 5 per cent. of this matter.

The author has for several years proceeded as follows:—
15½ lb. of naphthylamine are melted at 120° F. in an enamelled iron vessel, and mixed with 13½ lb. of nitric acid at 75° Tw. and an equal weight of water, the whole gently heated to boiling. This heating requires care and attention. If the fire is too strong a violent effervescence takes place and the whole may boil over; the mass may even take fire and be entirely destroyed. It is boiled for forty minutes and then poured into shallow, glazed earthenware vessels to cool.

The product should weigh about 34 lb., it is crystalline,

grey coloured outside, and dark brown in the interior; it can be prepared beforehand in quantity, as it is not injured by time if kept in closed vessels.

To make the colour, take $12\frac{3}{4}$ lb. of the nitrate of naphthylamine and dissolve it in about a gallon of acetic acid at 11° Tw., and mix the liquid with 4 gallons of warm starch paste at $1\frac{1}{2}$ lb. per gallon, and then add 11 oz. chlorate of potash dissolved in $\frac{1}{2}$ gallon of boiling water.

A reducing paste for this colour is made by adding 6 oz. of chlorate of potash dissolved in 3 pints of hot water to 2 gallons of warm starch paste.

If a small quantity of hydrofluosilicic acid be added to the colour before it is printed a very dark chocolate can be obtained, but it must be used in small quantities. The colour after printing is hung twenty-four hours in a warm, moist ageing room, where the temperature should mark about 75° F. on the dry bulb thermometer, and 72° F. on the wet bulb. Though the whites look all right from the machine they acquire a pink hue in the ageing, which is derived from naphthylamine communicated by the plain parts of the rollers, owing to the salts crystallizing in contact with the cold metal and the crystals being pressed by the doctor beyond the engraved parts. It is not unusual to find white crystals of naphthylamine under the doctor, and then the whites are found to be much stained. This inconvenience was obviated by warming the roller with hot water before commencing to print; and it is also desirable to keep the colour warm during printing.

After ageing, the pieces are chromed in a box with rollers, using at the rate of 60 lb. bichromate and 45 lb. hydrochloric acid at 34° Tw. for 100 gallons of water, or instead of the hydrochloric acid, the same weight of hydrofluosilicic acid may be employed. After washing, they are then passed for twenty minutes in chloride or hypochlorite of soda, and afterwards soaped for half an hour at 140° F., then washed, dried, and chlored.

The chocolate thus obtained is very good, it is fast to boiling soap and to acids, it gradually loses tone when exposed

to the air, and eventually becomes yellowish; it suffers much in beauty by finishing.

This colour can be combined with other fast colours, such as aniline black or lead orange. The aniline black goes through the same operations as the chocolate without any modification.

The orange is fixed by adding sulphate of soda to the acid chrome bath, then separately chromed and raised in hot lime, or the following variation may be used: Pass first in the acid chrome, wash and pass cold in ammonia water, then chrome and raise in lime.

This chocolate can also be printed with madder colours for dyeing, it withstands all the treatments of dunging, dyeing, and soaping, and seems to be stronger and better for them. Not much is said of this, however, as no results have yet been obtained on a large scale.

A purple can also be obtained from naphthylamine, and several years ago some pieces were printed with it, but although it is fast to boiling soap it loses much of its brightness by exposure to air, and it was given up. It was made as follows: In 4 gallons of starch paste, mix up 20 oz. of hydrochlorate of naphthylamine dissolved in 1 gallon of cold water, when required for use add 3 lb. of violet mordant at 72° Tw.; this mordant is composed of 13 oz. of acetic acid, 1¼ oz. of aniline purple in crystals, and 2 lb. of crystallized chloride of copper. After printing, the cloth was aged as for aniline blacks, and then it was only necessary to pass in an alkaline liquor to obtain a brilliant purple.

M. Lamy gives the following receipts for obtaining grey and drab shades from naphthylamine alone, or in conjunction with aniline.

No. 1.

2 gallons starch paste.

1 lb. crystals of muriate of iron, dissolved in
½ gallon water.

$\frac{1}{10}$ gallon of naphthylamine chocolate.

No. 2.

2 gallons starch paste.
1 lb. crystals of chloride of copper, dissolved in
 $\frac{1}{2}$ gallon water.
 $\frac{1}{10}$ gallon of naphthylamine chocolate.

No. 3.

1 gallon water.
3 lb. pale British green.
5 oz. chlorate of potash.
3 oz. salammoniac; boil, and when cool, add
 $2\frac{1}{2}$ oz. hydrochlorate of aniline.
13 oz. naphthylamine dissolved in
13 oz. acetic acid at 10° Tw.

and when wanted for use

$6\frac{1}{2}$ oz. crystallized chloride of iron, or, instead,
 $6\frac{1}{2}$ oz. of sulphide of copper in paste.

Cotton in skeins can be readily dyed with naphthylamine by following the same process as for printing. The only precautions required are to pass the cotton from the naphthylamine bath to the chrome bath without drying, then wash and repeat the passages until the desired shade is obtained. This process was put into practice some time ago, but the high price of the material and the insupportable smell of it caused it to be abandoned.

M. Lamy, in conclusion, expresses his belief that with a little more work upon this substance and more experience, it will eventually be found a valuable colour for the printer.

3. *Upon the Formation of Aniline Black.**

BY M. ANTONY GUYARD (HUGO TAMM).

ANILINE Black, from the time of its discovery, has strongly attracted the attention of both scientific and technical men;

* Read at the Meeting of the Industrial Society of Rouen, April 7th, 1876.
Bulletin of the Society, iv. p. 126.

for this fine *purplish black*, as it may be called, distinguished by its permanency, richness, method of production, and application upon textiles entirely revolutionised previous ideas, and opened a new field to scientific speculation and technological efforts. It was only after numerous and remarkably successful struggles with the apparently insurmountable difficulties which at first surrounded it that it has taken its proper place.

On the one hand, practice had the task of applying on fabrics a substance in itself destructive, and theory had to explain the attendant phenomena which were veiled in obscurity. It appears, however, that determined efforts are invincible, for nearly at the same time the scientific and practical workers had triumphed over their difficulties, and finally settled the great question which is our subject.

I will not here attempt the history of aniline black which is yet fresh in the memory of all. I shall confine myself to new facts which are little known, and which complete and clear up its history, or to others which have lately placed this splendid colouring matter in the first rank of tinctorial matters. I mean *vanadium aniline black*.

When hot and very concentrated solutions of an alkaline chlorate and muriate of aniline are mixed together, the mixture commences to boil, becomes thick and swells up, and finally projects in an explosive manner torrents of thick and suffocating vapours in all directions, accompanied by large clouds of an intensely black, but light and porous substance.

This black matter has all the external appearances of lamp black, for which it might be easily mistaken, but when it is collected, washed, and submitted to distillation, it yields gases and liquid products, among the latter, aniline with all its characteristic properties can be observed.

This product is therefore not lamp black, but aniline black. The experiment just described, though interesting and well calculated to give an audience a vivid idea of a volcano in action, does not seem to be of any practical application. It is however the same substance, as we shall immediately see, which colours the most delicate fibres of cotton with an unchangeable and indelible black.

If instead of taking hot and neutral liquids, as in the above experiment, we substitute cold, concentrated, but acid fluids, we shall observe in a few instants the clear liquid begin to darken, and then become thick, at the same time evolving abundance of chlorine and chlorinated products.

When the reaction is accomplished, the mass may be diluted with water and boiled; the characteristic greenish tint of the black disappears, it becomes more dense, and we have the aniline black, which being collected upon a filter, washed, dried, and distilled, behaves precisely as the product of the first experiment; it yields aniline and is distinguished by its insolubility in acids, alkalies, and alcohol, and by its indifference towards chemical reagents.

If fibres or cloth had been put into the mixture while the aniline black was being formed, we should find them dyed of a good black, but the textile matters so injured and weakened that all ideas of using this simple process for dyeing must be given up. However, it is clear that it is possible thus to dye, but it is not apparent how the process can be made practicable. We had the idea of diluting the liquids, but we saw the mixture underwent no change, no aniline black was produced.

These two experiments shew clearly that aniline black is the result of the action of the products of the destruction of chloric acid upon aniline, for if we analyze the phenomena we find we have at first acid combined with aniline and a base combined with chloric acid, and afterwards the oxygen of the chloric acid fixed upon the aniline which has been changed into black, and the chlorine of the chloric acid in great part set free.

In other words, *aniline black is the product of the incomplete combustion of aniline in chloric acid in the midst of a fluid.*

The phenomena of combustion by chloric acid in the midst of water are not new in chemistry. Every one knows the beautiful experiment made by placing at the bottom of a glass of water a few crystals of chlorate of potash with some fragments of phosphorus, and introducing by a narrow tube strong sulphuric acid upon the chlorate. Hyperchloric acid is

evolved, and the phosphorus burns with its usual brilliancy though surrounded with water.

The phenomena of combustion assume very varied aspects according to the nature of the combustible body; thus, if pieces of zinc are put into a concentrated solution of a chlorate and a little sulphuric acid added, the water is decomposed by the zinc, and the nascent hydrogen liberated, acts with such energy upon the chloric acid, which it decomposes, that the liquor boils rapidly without any trace of gas being formed. The ebullition can be maintained for hours together, and only ceases when either the chlorate or the zinc is destroyed. Under favourable circumstances this would be the most pleasant and economical method of warming which can be conceived.

If this experiment be varied by substituting organic matters for the zinc or the phosphorus, such as starch, extract of logwood, naphthylamine, methylaniline, toluidine, or aniline, the products of the oxidation are coloured substances of a marked tinctorial power which might be introduced in dyeing or printing.

Starch becomes lemon-yellow, but has no dyeing properties.

Logwood extract yields a substance which dyes silk of a fine golden-yellow colour, possessing great brilliancy.

Naphthylamine gives a very dark purplish-brown colour.

Methylaniline gives a dark purple.

Toluidine yields browns or bronzes of a coppery lustre, especially upon silk.

Aniline gives aniline black.

If we could contrive the decomposition of the chloric acid in dilute and nearly neutral solutions, we might expect to bring the reactions under control and ascertain what took place. We tried numerous additions to dilute solutions with the intention of bringing about the decomposition of the chloric acid; heat gave no results; with electricity we obtained some black, but it accumulated at the poles and we could not make any use of this method; lastly, we introduced chemical reagents, which may be divided into two principal classes, the reducing and the oxidizing.

With reducing agents we obtained no results, either they exercised no influence, or they acted too strongly by absorbing all the products of the decomposition of the chloric acid. The ferrocyanide of potassium, however, gave good results with the assistance of heat and time.

The action of oxidizing agents was too energetic, the fluids became thick in a few minutes, and when we examined the blacks thus produced we found they were not what we were in search of, but, on the contrary, organic bases soluble in acids with which they formed dark coloured salts, or soluble in alcohol which they coloured strongly.

We then introduced metallic salts into the mixture, which according to their degree of oxidation may act as either reducing or oxidizing agents, and which in contact with other reducing or oxidizing mixtures may alternately reduce the one or oxidize the other, and we now arrive at the point so long searched for.

Amongst the metallic salts the most remarkable is the chloride of vanadium. One part of this salt has the power of transforming 1,000 parts of muriate of aniline into aniline black, in the presence of alkaline chlorates.

This powerful action of vanadium is due to a curious property which it alone possesses in so marked a degree. It absorbs and gives up oxygen with equal facility, its reducing power being nearly equal to its oxidizing power. *It is a mineral ferment.*

The chemical part played by the mycoderms in fermentation is well known. These infusoria, described by Pasteur, take up oxygen from the air and transfer it to the sugar or alcohol, which are thus changed into alcohol and acetic acid respectively. Vanadium may be said to be the mycoderm of aniline, which it transforms into aniline black; but in this case the oxygen is not obtained from the atmosphere, but from the chlorates present. In a scientific point of view the phenomenon is identical with that of fermentation or slow combustion in the mass of the fluid, and in the special case we are considering the products of the fermentation instead of being alcohol and carbonic acid, are aniline black and chlorine.

The remarkable power of vanadium, as I have said, is this : It reduces oxidized bodies and becomes oxidized, it oxidizes reducing bodies and becomes itself reduced. In a mixture of muriate of aniline and an alkaline chlorate, it destroys the chlorate, itself becoming oxidized, and oxidizes the aniline while it is itself reduced. This is so exact that if an excess of either aniline or chlorate be present in the liquors, the excess will be found unaltered after the deposition of the aniline black. It should, consequently, be observed in practice that to prevent loss, the mixture should contain exactly two equivalents of muriate of aniline to one equivalent of chlorate.

Direct experiments made separately upon chlorates and muriate of aniline do not leave any doubt upon the explanation which I am about to give. The vanadous salts decompose chlorates with evolution of chlorine while they are transformed into vanadic salts; on the other hand, the vanadic salts or the vanadiates are instantly reduced to the state of vanadous salts by contact with muriate of aniline.

With very dilute fluids, as in the following example, the vanadium produces all the black that the liquor can furnish, and that in the cold and with great rapidity.

Water	1000 parts.
Muriate of aniline	40 „
Alkaline chlorate	15 to 20 „

The scarcity and consequent dearness of vanadium is the only obstacle to its immediate application in dyeing and printing; apart from this defect, which may be only temporary, vanadium is the best material for producing aniline black.

* * * * *

In dyeing, as well as in printing with vanadium aniline black, one is so perfectly master of all the operations, and can so easily vary the strength of the dye according to the nature of the fibre, that this reaction of vanadium should be considered as the final expression of science upon the method of producing this colour.

When the subject has been studied with care it is found that nearly all which is written by different authors is correct, and that aniline black can be produced under a variety of

conditions and under very different circumstances. Thus the contradictory assertions that aniline black *can be made* without a metal, and that it *cannot be made* without a metal, are as I have shewn equally true, only they are related to facts which are not of equal importance in practice. It may be added that the mixtures proposed by different authors give excellent results when vanadium is substituted for the metal or other intermediary proposed, and that all the recommendations made for the choice of salts and in the preparation and application of mixtures find their place when applied to the vanadium black. To give an example, I can confirm the opinion expressed that the richer the aniline is in phenylamine the more brilliant and beautiful are the blacks produced.

In theory, aniline black being the product of the destruction of chlorate of aniline, it would seem that there is little to say upon the point, and that all mixtures capable of forming chlorate of aniline would be equally good; but in practice it is evidently not so, and I hope some general considerations upon this point will be found useful.

There are found in commerce three kinds of muriate of aniline, the acid, the neutral, and the basic. Experience has shewn that the acid salts are to be avoided, they produce the black too quickly and have a tendency to weaken the cloth. The basic salts are also not good because they act too slowly and not regularly. In the basic salts the excess of aniline precipitates the oxide of vanadium, which becomes irregularly distributed throughout the mass and causes the formation of the black to be confined to certain points only. The neutral salt on the contrary possesses all the qualities necessary to give the best results.*

*The chemical committee of the Rouen Society append the following note:—The crystallized aniline salts of commerce generally contain an excess of hydrochloric acid in the free state. This inconvenience is obviated by a very simple method indicated by M. G. Witz. The starch paste to be employed for the vanadium aniline black is coloured with methylaniline purple (Paris violet), and after the muriate of aniline has been dissolved in the paste a quantity of rectified aniline oil is added sufficient to colour the whole of a reddish-violet; the colouring matter serves at once as a reagent to indicate the neutrality, and a sightening for the printer, which is necessary on account of the suppression of the sulphuret of copper. Prepared in this manner the colour keeps well and gives good and regular results.

The choice of the chlorate is not indifferent. The chlorate of potash, which is the most stable, is also the best, but it is not very soluble, and the crystallization which takes place gives rise to inconveniences. The chlorates of ammonia, lime, and in general the less stable chlorates are too easily decomposed. The chlorate of soda, which is at once very soluble and very stable, appears to be the preferable salt, and recommended by its valuable practical properties.

As to the state of the vanadium, any soluble vanadous or vanadic salt, or a soluble vanadate will answer, all being equally efficacious.

All the salts at a minimum of oxidation of those metals which possess two degrees of oxidation have a greater or less power of decomposing chlorates, and provided that they do not absorb too completely the products of the decomposition of the chloric acid, aniline black is formed. Thus the salts of iron and manganese, but especially, as I have observed, those of uranium, molybdenum, and tungsten, when at a minimum of oxidation, and the well known copper salts give excellent blacks.

The antimony salts at the minimum of oxidation absorb the whole of the decomposition products of the chlorates, and are not only incapable of producing the black, but even prevent its formation in colours containing vanadium.

It is easy to understand that in conjunction with a powerful agent like vanadium, the proportion of it might be greatly diminished, and its place substituted by a metal which could assist in the action, although by itself acting only in a feeble manner. Mr. Pinkney in his patent availed himself of this property, and claimed salts of nickel in conjunction with vanadium, for with $1/5000$ of vanadium, the nickel salts contribute strongly to the production of the black.

The chemical properties of aniline black are neither numerous nor remarkable. It is no doubt produced by the condensation of phenylamine, and is not derived, like a great number of the aniline colours, from the condensation of aniline and its homologues.

With phenylamine we obtain only emeraldine, the finest black it is possible to produce, while with the commercial aniline salts, containing 60 or 70 per cent. of aniline to 40 or 30 per cent. of toluidine and other alkaloids, we may always notice the simultaneous production of mauveine, violaniline, toluidine bronze, and the brown colours of cumidine and xylidine.

The character of emeraldine is that of being insoluble in the more powerful acids when diluted, while the accompanying coloured matters are soluble. From a practical point of view this is not important, for the very dark colouring matters spoken of soften the black without materially injuring its beauty; it is even possible to obtain various hues by adding at pleasure the salts of methylaniline, diphenylamine, or naphthylamine, or other alkaloids yielding very dark shades by oxidation through chlorates.

Emeraldine, which always forms the basis of the true aniline black, shews the double properties of a weak acid and a weak alkali. With oxides it gives dark blue salts, or with acids dark green salts; and like emeraldine these salts resist the action of chemical agents. Bichromate of potash acts, however, very energetically upon it, producing mauveine or an analogous compound, this action is made use of to correct the greenish tint of the aniline black.

Emeraldine has the curious property of being dissolved and destroyed by the yellow sulphide of ammonium, while the colours which usually accompany it are not so influenced.

This important reaction combined with the unequal action of acids and alcohol upon the various matters constituting aniline black, enable us always to investigate the composition of a particular colour.

The true aniline black is emeraldine, dehydrated either by boiling or drying at a temperature between 95° F. and 212° F. In the dehydrated state emeraldine is only feebly acted upon by the yellow sulphide of ammonium, and then constitutes the true typical aniline black, which ought to always be the basis of the general aniline blacks.

In the minutes of the meeting of the Chemical Section of the Industrial Society of Rouen, 25th February, 1876, the following occurs:—

Mr. G. Witz exhibited to the section specimens of aniline black from vanadium. He stated the quantity of vanadium required to induce the rapid formation of this colour was so exceedingly small, that there was a real practical advantage in replacing the sulphide of copper paste by it. At the present time, and notwithstanding the very high price of vanadium (about three times the price of gold (!), the use of such minute proportions of this metal shewed a saving of 50 per cent. of the value of the sulphide of copper as used in the regular aniline black for printing.

The results, practically obtained upon a good number of pieces, are superior to those from the ordinary process, both for beauty and intensity of colour, as well as for the facility with which they are obtained.

Analysis of Aniline Black.

M. R. Nietzki communicated a paper to the Berlin Chemical Society upon aniline black, which is printed in the May number of the "*Berichte des Deutschen Chemischen Gessellschaft*," p. 616., from which we abstract the following account.

The aniline employed was made from chemically pure crystallized benzol; it had a constant boiling point at 182° C., and gave no fuchsine reaction when treated with bichloride of mercury. The materials employed to produce the black were 20 grammes chlorate of potash, 30 grammes sulphate of copper, 16 grammes salammoniac, 40 grammes hydrochlorate of aniline, and 500 c.c. of water; these were heated to about 60° C. The liquid, after the reaction, during which an odour of chloropicrin was observed, changed into a dark green mass. When a purified and recrystallized aniline salt was employed, this smell of chloropicrin was absent, or only perceived very faintly, and it was believed to be due to a trace of nitrobenzole in the salt. An addition of hydrochloric acid hastens the reaction. The solid matter was treated with dilute hydrochloric acid, then dried,

ground up, and again treated with various solvents; benzol, ether, petroleum spirit, and alcohol. Afterwards digested with alcohol containing hydrochloric acid, which removed a considerable quantity of a brown substance. The powder remaining was lustreless and dark green in colour.

According to Reineck this is the hydrochlorate of a base which he has called "nigranilin."

The dark green powder becomes dark violet by the action of alkalies, and the so-named base upon drying forms a dark powder with a metallic lustre. Heated alone, or with soda-lime, it yields a basic distillate, in which the smell of aniline can be observed.

M. Nietzki found that both the hydrochlorate and the base were soluble in aniline, and he purified his products by solution and precipitation with acid, and finally obtained but 1 gramme of matter from 1000 grammes of aniline.

After the statements in the last paragraph it seems to us that very little interest attaches to the results of the analysis. An aniline black, soluble in aniline, and of which only 1 part was obtained from 1000 parts of aniline, can hardly be the substance which dyers and printers are so much interested in.

The formula of the hydrochlorate deduced from several analysis was $C_{18} H_{15} N_3 HCl$.

4. *M. Michel de Vinant on Dyeing, Printing, and Bleaching.**

THE sub-acetate of lead referred to is made by taking 6 gallons of water and dissolving in it at the boil $22\frac{1}{2}$ lb. of acetate of lead and $12\frac{1}{2}$ lb. of litharge in fine powder.

Ponceau, or Poppy Red, on Silk.—Use cochineal liquor at 4° Tw. To 5 lb. cochineal add 12 oz. measure of the tin solution below, and dye. Twenty-four hours are required

*Continued from vol. i., p. 290.

to get the colour. After dyeing, leave the silk covered twelve hours; then wash lightly, brighten with lemon juice, and dry. This colour is weighted with white sugar dissolved in water; coarser shades are weighted with galls before dyeing. Honey is also used to give weight.

The solution of tin is made from 4 lb. muriatic acid, 2 lb. nitric acid, and $3\frac{1}{4}$ oz. of tin dissolved gradually.

Another Method for Poppy Red.—Prepare the silk in the stannate of soda below, pass in sulphuric acid, and wash well; then give the alumina mordant below at 8° Tw., thickened with British gum at 1 lb. per gallon. Dry with the mordant and hang up for twenty-four hours at least; wash out well and dye in cochineal; when the dye is well up, add nitrate of tin and brighten to shade required. By this method as good colour can be obtained as by the other and at less cost. The British gum is added to the alumina mordant to facilitate the washing off, it being a property of alumina to render fibres more or less waterproof.

The stannate of soda for the above is made from 7 lb. of oxymuriate of tin and 3 gallons of caustic soda at 35° Tw., to which mixture is added 1 lb. of oxalic acid dissolved in 1 gallon of water. Reduce to 4° Tw. and use cold.

The alumina mordant is made by precipitating 1 lb. of alum dissolved in half a gallon of water, by 1 lb. of crystals of soda dissolved in a quart of water, the precipitate collected on a filter and dissolved in 1 quart of strong acetic acid.

Fuchsine Red on Silk.—Acidify the water with tartaric acid add the colouring matter, and dye cold; give a brightening after dyeing (with tartaric acid?). To dye a violet shade, first give a bottom with Hoffmann's violet or red violet, according to the shade required, and finish with the fuchsine. The violet and the fuchsine might be dyed up together, but the result is not so good.

To obtain a yellowish shade approaching to scarlet, dye the silk yellow first.

French Blue for 40 lb. Silk.—Give nine ends in a mixture of 60 gallons water heated to 120° or 130° F.; 9 lb. of nitrate of iron at 100° to 130° Tw., and 1 lb. 10 oz. salt of tin; wash

well and give nine ends in a mixture of 60 gallons warm water, 2 lb. prussiate of potash, and 1 lb. of sulphuric acid; and then, without washing, give nine ends in the first bath, wash out well, and give nine more ends in the second; then freshen up the first bath with 2 lb. of nitrate of iron at 60° Tw. and 10 oz. of salt of tin, give nine ends, wash well, and give nine ends in the prussiate bath freshened up with 12 oz. of prussiate and 1 lb. of sulphuric acid, wring and leave in a covered mug for five or six hours, wash, brighten, and dry in the air.

Fancy Shades on Silk.—In silk dyeing, as in cotton, all the colouring matters can be employed; and for darkening or saddening, mixtures of iron salts and alum with extract of indigo, cochineal, fustic, &c.

All the fancy shades can be made by mixtures of the various aniline colours, but unfortunately they are very loose. Some dyers use them with the addition of cochineal and other colouring matters. For light shades it is best to use mixtures of extract of indigo, fustic, and cochineal; the colours from these have at least some power of resisting the action of air and light.

These colours are usually dyed cold, and the silk very rarely mordanted beforehand. The mordant used is little more than an acid, and is mixed with the colouring matter in the dye vessel. To weight such silks honey and white sugar are employed.

No exact proportions can be prescribed on account of the dyer having to match a certain shade given to him.

Ammoniacal Cochineal.—For 5 lb. of silk take 5 or 6 gallons of water, and prepare the bath with 1½ oz. tartaric or ¾ oz. sulphuric acid, and ½ gallon of solution of ammoniacal cochineal at 2½° to 3° Tw. After dyeing, the silk may be weighted to the extent of 10 or 15 per cent. by adding dissolved sugar or honey to the dye liquor.

Sky Blue is given with extract of indigo acidulated with sulphuric acid, and light yellow with picric acid in a bath also acidulated with sulphuric acid.

Grey.—For 5 lb. of silk, make a mixture of 1 oz. of tartaric

acid or other acid with $\frac{1}{2}$ gallon of ammoniacal cochineal at $2\frac{1}{2}^{\circ}$ or 3° Tw., $\frac{1}{2}$ oz. of extract of indigo, and about $\frac{1}{4}$ oz. of picric acid, each ingredient being separately well dissolved before the silk is entered. Other shades of grey can be obtained by changing the proportion. Mr. Vinant remarks:—"Scientific men have given thousands of receipts and tried to establish some fixed proportions. After all their instructions it is found out that there is nothing fixed, and for a very simple reason. If you work in the same locality where they have worked, and with the same materials, it is evident you will obtain the same shades. But no one who consults a book is in that position. It is therefore only in connection with common colours that any proportions can be given which have a claim to exactness. For light and fancy shades the proportions given can only be approximative."

"Even in printing, notwithstanding the systematic precision with which all the processes are carried on, there is found at times an irregularity which is very puzzling to the colourist. In order to give you an idea:—I was once at Rouen in a considerable printworks where the colourist had been eighteen years, and for some years they had given up working a certain style. This style was wanted one day again, but the colourist only produced it in a very imperfect manner. M. B——, the proprietor, in speaking with me expressed his astonishment, telling me that formerly the colourist, M. R——, had done this style very well. You see that even after a colourist has been eighteen years on a works he has his difficulties." There is a good deal of this familiar style throughout M. Vinant's book.

Dyeing of unspun wool.—This dyeing referring chiefly to aniline colours, we give an abstract of the author's remarks upon making and using solutions from the solid colouring matters, and these details are from the printed instructions of a Lyons house.

Solution of aniline colours.—The alcohol used for dissolving those aniline colours not soluble in water, should be of a good quality, strong, and quite free from fusel oil or amyl alcohol, which is very injurious to the colours. Alcohol containing

fusel oil is known by its peculiar odour, and by becoming milky when mixed with water.

Methyline or wood spirit of good quality can also be used as a solvent; acetic acid is also employed in mixture with alcohol or wood spirit, it should be free from sulphuric acid.

In dissolving aniline colours in water, the water should be boiling, and the powdered colouring matter added gradually as fast as it dissolves, boiling water poured on a mass of colour causes it to become lumpy and to dissolve badly; if naked fire is used to heat the vessel of water, there is risk of melting and injuring the colouring matter.

Dissolution in alcohol is best made in a close vessel heated by steam, but any narrow necked vessel will answer, and evaporation of the alcohol can be prevented by fixing a glass tube 5 feet long, in the neck by means of a cork; if the liquor rises into this tube the heat must be withdrawn.

Good filtration of the solutions is a very important matter in order to avoid stains in dyeing; the filtering material may be either felt or paper. The insoluble matter left on the filter must be put back again to be boiled up; in the case of blue colours the purest part is the last to dissolve, any considerable residue on the filter only shews that there has not been enough of alcohol employed.

The alcoholic solutions keep very well, but as there is nearly always a deposit of colouring matter in the vessels which have stood for some time, they should be always warmed up by placing in hot water before using. If this precaution is neglected, the deposited colour floats on the surface of the dye bath, where it forms a greasy or tarry spot which will give a stain on the cloth.

It sometimes happens that the colouring matters in tin boxes are exposed to considerable warmth, and in some cases fuse together into a solid mass, and in others form a pasty mass, this is simply an effect of heat and does not injure the colour. To dissolve such colours properly, they should, when cool enough, be reduced to fine powder.

Fuchsine is dissolved directly in hot water, somewhat less than 1 oz. of crystals to a gallon of water, or the crystals can

be placed on a filter and boiling water poured upon them. A water containing lime should not be employed for fuchsine, as it makes the solution difficult and liable to change. Fuchsine should only be dissolved as it is required.

The soluble blues are dissolved in boiling water, 1 lb. of blue to 3 or 4 gallons of water, filtered. A stock of this solution may be prepared; it does not require warming up before using.

The Lyons blue is dissolved by taking at the rate of $2\frac{1}{2}$ gallons of alcohol, $1\frac{1}{2}$ oz. of sulphuric acid, and 1 lb. of the reddish blue. The *blue lumière* or T blue, requires for 1 lb. 3 to $3\frac{1}{2}$ gallons of alcohol, and about 2 oz. of sulphuric acid, the whole is boiled for half an hour.

Red violets are dissolved in the proportion of 1 lb. in $1\frac{1}{2}$ gallons of alcohol, and $\frac{9}{10}$ gallon of acetic acid, boil gently for about a quarter of an hour.

Blue violets are dissolved at the rate of 1 lb. to $2\frac{1}{2}$ gallons of alcohol, without any acetic acid.

Hoffmann's blues or purples are dissolved in alcohol alone, in the proportion of 1 lb. to 2 or $2\frac{1}{2}$ gallons.

Preparation of Wool for Dyeing.—Sulphured wools must be treated with bran water or very weak alkaline water, or else the sulphur will turn fuchsine colours purplish, and make blues and purples grey and flat.

The wool must be quite freed from grease by treatment with soap and soda, and well washing. If the wools are very rich some tartar may be added to the dye, otherwise the dyeing is done without any addition, the shade being pushed somewhat high. After washing the goods are lightly sulphured; a part of the colour is thus destroyed, but what remains is very fast. Fuchsine colours thus dyed stand fulling very well, but blues and violets cannot be depended upon.

Mordanting.—All sorts of woollen goods which have to be fulled after dyeing require to be mordanted by the following process, in order to prevent loss of colour and stains.

For a piece of say 65 yards, weighing say 45 lb., dissolve, for heavy goods, as cloths, velvets, etc., 9 lb. purified sulphate of alumina, $5\frac{1}{2}$ lb. sulphuric acid, and $\frac{1}{2}$ lb. tin crystals, in a sufficient quantity of water brought to the boiling point, and

keep the goods in from fifteen to forty-five minutes, according to their nature, and the degree of fulling they will require, then hang them up to cool. For light stuffs, flannels, etc., one half the sulphate of alumina and tin crystals may be left out, and for loose wool the tin crystals altogether omitted. The mordanting liquor is cooled down and used afterwards for dyeing. As before said, fuchsine colours do not require this treatment, which is only for blues and violets.

Chromate Black.—For 50 lb. wool add $1\frac{3}{4}$ lb. muriatic acid to a sufficient quantity of water, heated to 104° F, work the wool in fifteen or twenty minutes and take out. Run away about one-half the acid liquor and add 40 measures of logwood liquor, made by boiling 40 lb. of logwood for every 100 lb. of wool. Enter the wool again, boil one hour, take out, drain, and leave for twelve hours covered up; then proceed to the raising, made by taking 12 oz. bichromate of potash and $1\frac{1}{2}$ lb. sulphate copper dissolved in cold water, work the wool cold for an hour, then raise to the boil and work for two hours, and finish by working for fifteen or twenty minutes in a bath made by dissolving in water at 104° F., $1\frac{1}{2}$ oz. sulphuric acid, 4 oz. tartar, and $\frac{3}{4}$ oz. turmeric; wash and dry.

The finishing treatment may also be made in a liquor containing 4 oz. sulphuric acid, and $\frac{3}{4}$ oz. turmeric without the tartar.

Another Black for Loose Wool.—For 10 lb. wool take

- $\frac{1}{2}$ lb. sulphate of soda.
- 1 oz. alum.
- $\frac{1}{4}$ lb. sulphate of iron.
- $\frac{1}{4}$ lb. sulphate of copper.
- 5 oz. dry extract of logwood.

Dissolve in boiling water, enter the wool and boil for seventy-five minutes, then rinse and finish by adding 2 to 3 oz. of sulphuric acid to the bath, or as much as is required to turn the logwood to a yellowish colour; add fustic if the shade wanted demands it, and wash well.

Black with Tin Mordant.—For 10 lb. wool dissolve in boiling water

$\frac{1}{2}$ lb. sulphate of soda.

1 oz. alum.

12 oz. oxymuriate of tin.

4 oz. sulphate of iron.

1 oz. sulphate of copper.

Boil for seventy-five minutes, lift, drain and wash; dye in logwood with a little fustic and sulphate of soda, and wash.

Fuchsine or Magenta on Wool.—It is quite unnecessary to mordant, but the wool must be free from grease. The dyeing is commenced cold, and the heat gradually brought up to 140° F., and must not go higher than 160° or 170° F. The wool is not washed after dyeing.

To obtain a yellower shade, resembling scarlet, the wool must be first dyed yellow and afterwards dyed with the fuchsine.

To have a violet or crimson shade make the water just acid with tartaric acid and add a small quantity of Hoffmann's purple.

If the temperature of boiling causes the colour to be injured, let the liquor cool and keep the wool in about twenty minutes, the colour will then come up right. One ounce or rather less of fuchsine will dye 10 lb. of wool.

Lyons Blue on Wool.—The wool being mordanted (p. 24), and the mordanting liquor being cooled down to 130° or 140° F., the colour is added in two separate portions, and the liquor raised to the boil and kept so about an hour to obtain a good and fast shade. Half an hour is sufficient for loose wool and light stuffs. Wash the goods.

Dark Blue.—To imitate Prussian blues on flannels, cloth, and velvet, it requires about $1\frac{1}{2}$ oz. of the blue ES. to 10 lb. of stuff. To obtain a dark navy blue, when the aniline blue has been quite taken up by the cloth, add a little logwood liquor, and an ounce or two of extract of indigo to the liquor, and keep the wool in. When the goods are to be severely fullered after dyeing, it is necessary to use the blue soluble in alcohol, in other cases the cheaper blue, soluble in water, will suffice.

Nicholson's Blue.—For a sky blue, upon 10 lb. of wool, about $\frac{1}{2}$ oz. of Nicholson's blue, and the same quantity of

borax is required; after dyeing, raise in sulphuric acid and wash.

Aniline Purples.—Sometimes the purples, and especially the reddish purples, do not dye up even colours, because the colour seems decomposed by the heat, the reddish part falling to the bottom of the dye vessel and thus separated from the blue part. To avoid this inconvenience, it is best to commence by adding about 12 oz. of common salt and a few drops of ammonia to the bath for every pound of wool, boil for half an hour, and regular results will be obtained.

Proceed in the dyeing as for the Lyons blue, but not heating so strongly, especially for the redder shades, and the bath should not be so strongly acidulated. Heat according to the shade required, acting upon the knowledge that the hotter the bath the bluer the shade, and the cooler the redder. If the shade is eventually too blue, let the bath cool, and keep the goods in motion. It requires $1\frac{1}{4}$ to $1\frac{1}{2}$ oz. of violet for 10 lb. of wool.

Hoffmann's Purple.—For the red shades same dyeing as for fuchsine, and for the blue shades same as for aniline purples.

[To be continued.]

5. *Critical and Historical Notes concerning the Production of Adrianople or Turkey Red, and the Theory of this Colour.**

BY THEODORE CHATEAU.

Corresponding Member of the Industrial Societies of Mulhouse and Amiens, etc. etc.

THIS portion of M. Chateau's memoir treats of the oil used in Turkey red dyeing, and the various processes of preparing the oil. Not all the fixed oils, whether vegetable or animal, are fitted for use in Turkey reds. Those generally employed are the olive oils, obtained for the most part from the Levant, Italy, or Central France. They are known under the name of

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Continued from Vol. i., p. 397, *Textile Colourist*.

huiles tournantes, or emulsive oils, which indicates their property of being miscible with weak alkaline solutions producing a milky emulsion.

The emulsive olive oil (we shall see presently that it is possible to make all kinds of oil emulsive) is a mixture of various low qualities of olive oil, containing mucilaginous matters, and which dissolves completely in an alkaline fluid; those kinds are most valuable which give the most perfect emulsion, in which the fatty matters remain longest without separating from the liquid.

Pelouze says that to distinguish an emulsive oil from an ordinary burning oil, one or two drops may be let fall into a test glass containing a solution of caustic soda at 2° to 3° Tw. The emulsive oil becomes opaque while the other remains transparent. This is the test, he says, usually applied by the dealers in these oils, and they judge the fitness of the oil from the degree of opacity of the oil drops.

M. Bolley, of Zurich, has the following remarks upon this subject:—To test the oil, mix 20 grammes of it with ten times its volume of a solution of potash at 6° Tw.; several samples of oil may be tried at the same time, and should be compared with a standard sample of known excellence. The oil is mixed up with the potash solution; a good oil forms a dense milky fluid, with a firm and persistent froth. Inferior qualities give a light fluid, blueish or yellowish, translucent, and with a light froth, which speedily breaks up. The tests are left at rest for twenty-four hours, and inspected again. During this lapse of time there should not be any appearance of large oil drops upon the froth, the froth should not have a curdy look, and below, the liquid should not be thin or blue-coloured, all of which are signs of a bad quality of oil. If the froth is made up of small vesicles which remain with persistence, and only very small globules of oil can be perceived upon it, and if all the liquid is white and dense, it may be concluded that the oil is of good quality. Medium qualities, of course, shew characters between those just indicated.

The oils most in use are vegetable fluid oils. In Greece

and Russia fish oils are used, and in India some solid vegetable fats are employed. Those oils which are most suitable for Turkey red dyeing being expensive, efforts have been made to communicate the emulsive property to lower priced oils by various means, as by incorporating yolk of egg with them, oxidizing them by nitric acid or alkaline hypochlorites, or by additions of fatty and sulphated fatty acids.

We will treat the methods of manufacturing emulsive oils in their chronological order.

Persoz, senior, in his well-known treatise, gives the following process for making an artificial emulsive oil: he says it is not difficult to make an oil emulsive, all that is required is to mix the yolks of two eggs in one litre of oil and leave it to itself; after a while the oil thus treated produces an emulsion when mixed with carbonates of either potash or soda, and acquires all the properties necessary. Other oils than olive oil can thus be employed.

The natural emulsive oil is always thick, and has a constant acid reaction, with a rancid taste and smell. According to Dr. L. Kaiser it was prepared, at least in Naples, by the expression of fermented olives which had been kept a long time, and consequently had become rancid. About the year 1840 many attempts were successfully made at Elberfeld and elsewhere to communicate the emulsive property to ordinary olive oil, and the process was kept secret for many years. Towards the end of 1846 Dr. Kaiser had occasion to examine many samples of olive oil, emulsive and ordinary, and at the same time to endeavour to discover a method of preparing the emulsive oil. A series of experiments led this chemist to the following results:—

(1.) Perfectly pure and non-emulsive olive oil was exposed in porcelain and metallic dishes for twenty-four hours to a temperature of from 113° to 131° F., and then left for another twenty-four hours at the ordinary temperature of a room and exposed to atmospheric action.

Tested with alkaline solution the oil which had been in the porcelain vessel was found unaltered, while that in the metallic

dish was partly but not completely emulsive. The effects were more decided after the oils had been heated to boiling for ten minutes and then cooled.

(2.) Forty grammes of pure olive oil were boiled with an equal weight of water, acidulated with 1 gramme of strong sulphuric acid; the mixture was in a porcelain vessel and the boiling was continued for two hours with constant agitation, and afterwards the mixture left for six days in a place heated to between 113° and 131° F. This oil furnished an emulsion with caustic potash, which after eight hours did not shew any trace of free oil in the creamy mixture. A repetition of the experiment in which the mixture was boiled by a current of steam, yielded an oil which gave an emulsion which shewed no signs of separation after remaining two days at rest.

(3.) The oil boiled up with steam as indicated in the preceding experiments, was immediately afterwards divided into four equal portions and mixed with *oleic acid* in the following quantities:

- | | |
|------|---|
| (1.) | 90 grammes of oil with $\frac{1}{2}$ gramme oleic acid. |
| (2.) | " " " 1 " " |
| (3.) | " " " $1\frac{1}{2}$ " " |
| (4.) | " " " without oleic acid. |

These mixtures were heated to from 167° to 185° F., and tested after ten hours' heating. The result of the trials shewed that the experiments 2 and 3, gave a perfectly emulsive oil, and the first was less perfect, and 4 the least perfect of all. No. 2 was the best.

(4.) Oleic acid added in the same proportion to fresh oil which had not been boiled, gave equally good results after the mixture had been exposed for twenty-four hours to a temperature ranging from 167° to 185° F.

The use of stearic acid, extract of saturn(?), etc., did not give in Dr. Kaiser's hands good results, that is the oil did not become emulsive. This chemist concludes the account of his experiments by saying, "We have therefore two methods of rendering oil emulsive and fit for using in the preparation of oil baths."

(1.) By mixing 1 part of oleic acid with 90 parts of ordinary oil, and keeping the mixture heated for twenty-four hours between 167° and 185° F.; if oil which has been boiled by steam with acidulated water be used, six hours' heating are sufficient.

(2.) By mixing 100 parts of oil with an equal weight of water, mixed with 3 parts by weight of sulphuric acid, keeping the mixture at boiling heat by means of steam for two or three hours, and after that maintaining the temperature at 167° to 185° F. for a period of forty-eight hours.

Pelouze, in 1856, made a communication to the Academy of Sciences of Paris upon emulsive olive oils; he does not appear to have been acquainted with the experiments of Dr. Kaiser, but confirmed his discovery of the existence of fatty acids, oleic and margaric in the emulsive oil. The proportion varied from 5 to 15 per cent., while in the olive oil used for food the fatty acids were either totally absent, or present only in very insignificant quantity. M. Pelouze further examined some artificial emulsive oils then in commerce, and among others those made by Boniface Frères, of Rouen, he found in them considerable quantities of oleic and margaric acid. M. Pelouze observes, "the reason why olive oil is almost exclusively employed in the Turkey red trade, is because the olives more readily undergo the changes which give rise to fatty acids than do the seeds which yield other oils, but as the nature of this oil is now (1856) well understood, it is easy to substitute for it lower priced oils such as colza, sesame, poppy, or palm oil. It is sufficient to crush the seeds or nuts containing the oil and to leave them a certain time before extracting the oil. Another and simpler method consists in adding directly to the ordinary oils a small per centage of the oleic or margaric acid, obtained from the manufacture of stearine candles."

The last method recommended by M. Pelouze was put into practice at Steiner's, near Manchester, where it gave good results.

Colza oil, with addition of oleic acid, was employed at Bar-

le-Duc, by Henry and Sons, for Turkey red yarn, and gave as good results as olive oil.

In 1856, Wilson and Walls proposed the use of pure oleic acid as a substitute for emulsive olive oil.

Mercer and Greenwood's Prepared Oils.—The so-called sulphated oil was prepared in the following manner:—One part, by measure, of strong sulphuric acid was incorporated with 8 parts of olive oil, and the mixture frequently stirred for eight days; water was then added, in which the mixture dissolved, and then common salt was added, which caused the oil to separate, so that it could be drawn off clear. The oil was afterwards oxidized by mixing it up with nine times its volume of hypochlorite of soda, made by adding carbonate of soda to solution of bleaching powder. The mixture was heated up by steam, and boiled until it lost its bleaching power, as tested by pale indigo coloured cloth; or, instead of heating, dilute sulphuric acid was mixed with it by small portions at a time, and the operation was considered complete when the mixture had no bleaching action. Other methods of oxidizing the oil are given in the patent, as exposing to the action of a current of heated air for several days; the mixture of the oil with bran water, or with sulphate of copper and common salt, and then forcing hot air through it; adding chlorate of potash or bichromate of potash to the original mixture of oil and sulphuric acid, or using nitrate of soda in the same manner. The patent in which these processes is described is dated June 22nd, 1846.

Bernard's Oxidized Oil.—M. Bernard, of Mulhouse, prepares oxidized oil by heating 15 lb. of linseed, or any other drying oil, to near the boiling point of water, and adding 2 lb. of finely powdered chlorate of potash, and 1½ lb. of oxalic acid by small portions at a time. At each addition there is an active effervescence. When all the salts have been added, the mixture is boiled for two hours. The oil thus prepared can be employed to treat cloth or yarn, either directly or by being mixed with alkalies.

Bance's Process for Oils.—The new processes of M. Alfred Bance consist;—

(1.) In heating the oils in contact with air, water, or vapour of water, so strongly that the foreign matters coagulate, and that a partial decomposition of the oil takes place.

(2.) In exposing the above oil, clarified by settling, upon an extended surface to the simultaneous action of air or pure oxygen, artificial heat, and solar light.

The manner of proceeding was as follows:—

A large vertical cylinder, made of enamelled iron, was three parts filled with oil to be acted upon, which might be rape seed oil alone, or mixed with linseed oil, palm oil, or fish oil. Steam, superheated to a temperature of 480° or 570° F. was then forced through the oil, and by the heat the vegetable matters were coagulated, and the oil itself partially decomposed. The change could be further advanced by forcing air heated to 480° F. into the oil.

As the change in the oil is only gradual, it is necessary from time to time to take samples from it for testing, and when it is found that the oil makes a perfect emulsion with six times its bulk of a weak alkaline solution, it is considered finished, and drawn off into cisterns to cool down.

The oxidation of the oil is effected by any contrivance which causes it to expose a large surface to the action of air and light while it can be kept warm; as, for example, a number of flat surfaces connected by channels or pipes, and the oil, pumped up from a reservoir in a heated state, flowing over these surfaces and thus becoming exposed to the air and to light. In favourable circumstances eight or twelve hours' exposure are sufficient to oxidize the oil, which then can be stored up for use. Such oil is equal or superior to the ordinary emulsive oil.

[*To be continued.*]

6. COLLECTED RECEIPTS.

COLOURS FROM CATECHU.*

No. 123. Catechu Brown for Garancine.

40 gallons catechu liquor at 16° Tw.—200 lb. gum Senegal—75 lb. salammoniac; heat until dissolved— $3\frac{1}{4}$ gallons red liquor at 11°—5 gallons acetate of lime at 22°—18 lb. nitrate of copper at 100° Tw. This colour is long known to me, and always worked very satisfactorily with dark chocolate; it contains only a small proportion of copper, but ages up well.

No. 124. Catechu Brown for Madder, 1848.

1 gallon acetic acid at 8°—2 quarts water—10 lb. catechu— $2\frac{1}{4}$ lb. salammoniac; boil and let stand twelve hours, pour off from the bottoms, add 2 gallons gum substitute water— $1\frac{1}{2}$ pints red liquor at 16°— $1\frac{1}{2}$ pints nitrate of copper at 70°.

No. 125. Catechu Brown for Garancine.

12 lb. catechu—12 lb. salammoniac—5 gallons water—1 gallon vinegar—2 gallons acetate of lime at 30°—boil until dissolved, strain, thicken with gum Senegal, and add 2 lb. muriate of copper at 50°—1 gallon red liquor at 10°. This colour yields a pleasant and very yellowish shade of brown.

No. 126. Catechu Brown for Madder or Garancine.

60 lb. catechu—2 gallons acetic acid at 8°—11 gallons water—2 gallons of molasses—boil and make to 20 gallons—

*Continued from Vol. i., p. 115. This collection is continued at the request of several correspondents, but in accordance with the advice of some respected practical friends, the plan is somewhat changed, and some selection exercised; so that instead of giving very similar receipts, though obtained from widely separated sources, it will be sought only to give those which have some distinct differences in them. The Editor does not hold himself answerable either for the accuracy or goodness of the receipts. They are all from reliable sources, many of them are of proved excellence, and it is hoped that the collection, when complete, will be both interesting and useful for reference.

18 lb. salammoniac—72 lb. gum gedda—2 gallons muriate of lime—boil, strain, and add 1 gallon nitrate of copper at 88°—1 gallon acetate of copper below.

No. 127. Acetate of Copper for No. 126.

18 lb. sulphate of copper—12 lb. brown sugar of lead—3 gallons of boiling water.

No. 128. Catechu Brown for Garancine.

90 lb. catechu—13 lb. salammoniac—10 gallons water, boil, strain, and add 15 gallons thick Senegal gum water, 4 gallons nitrate of copper at 82°—2½ gallons acetate of copper. Can be reduced by increasing the amount of gum water, and if required, red liquor added.

No. 129. Catechu Brown for reducing.

15 lb. light yellow, and 15 lb. dark brown catechu—2½ gallons wood acid—6 gallons water—15 lb. salammoniac—boil, strain, or settle, and add 2¾ gallons acetate of copper at 2½ lb. per gallon—20 lb. gum—½ gallon red liquor. This can be reduced for two or three browns by means of thin gum water, adding up to one-eighth part of red liquor.

No. 130. Catechu for Brown in Dipped Indigo Styles.

2½ gallons catechu liquor at 16°—1¼ gallons strong mordant—18 lb. of gum in powder. The mordant is composed of 8 gallons water—20 lb. verdigris—5 lb. salammoniac—60 lb. nitrate of copper. This is for the so-called neutral or lapis style, containing mordants for madder, and will not stand more than about four or five minutes' dipping; chromed warm, dunged, and dyed in madder or garancine. Red liquor may be added if the shade required needs it.

No. 131. Dark Brown for Steaming and Chroming.

20 lb. catechu—7 gallons water—25 lb. gum—4½ lb. crystals of acetate of copper—2¼ lb. cream of tartar—3 gallons water. Can be reduced for a second shade.

No. 131. Catechu Brown for Garancine.—Penney.

6 gallons water—38 lb. catechu—18½ lb. salammoniac—1½ pints acetic acid, this forms the standard—take 8 gallons of

the standard—2 gallons gum water— $1\frac{1}{4}$ gallons Penney's fixing liquor—1 gallon red liquor. Penney's fixing liquor was patented about 1863; it consisted of muriatic acid saturated with lime, and to the hot muriate of lime one-fifth of its bulk of nitrate of copper at 80° Tw. was added.

No. 132. Catechu Brown with Borax.—*Penney.*

20 gallons water—60 lb. catechu—6 oz. borax—boil well for eight hours—take 16 gallons of the above liquor at 15° —2 gallons acetic acid—32 lb. salammoniac—to 3 measures of this standard add 1 of gum water and half a measure of Penney's fixing liquor, see above. The borax, which was thought to cause a more perfect solution of the catechu, could not in the above quantities be of much use.

No. 133. Catechu Brown for resisting Purple.

16 lb. catechu—8 lb. salammoniac—4 gallons lime juice at 8° —5 lb. measure nitrate of copper at 84° —3 lb. acetate copper solution—24 lb. gum Senegal. The ordinary catechu brown without any acetate will resist light purples if taken out to the dye soon; in the receipt the lime piece is probably too strong and the colour would be bad to work.

No. 134. Catechu Brown with Starch, 1832.

4 lb. water—1 lb. 2 oz. catechu— $\frac{1}{2}$ lb. acetic acid—boil, and add $17\frac{1}{2}$ oz. acetic acid. Thicken the liquor with starch at $1\frac{1}{2}$ lb. per gallon, and when cold, add 4 oz. nitrate of copper. I have given this receipt because it is the oldest that I know of for this colour; I got it from an English receipt book in MSS., but the weights of 1 lb. 2 oz. and $17\frac{1}{2}$ oz. being the equivalents of $\frac{1}{2}$ a kilogramme and $\frac{1}{2}$ a litre shew that it was originally from the French. The following receipt is also inserted as being old and dating soon after the application of catechu in dyed styles.

No. 135. Old Catechu Brown.

Standard; 4 lb. catechu—2 quarts of vinegar—5 pints acetic acid—15 oz. salammoniac—1 quart acetate of copper, use the clear. Take 2 quarts of the standard—1 quart of

water—6 oz. red liquor and thicken with 14 oz. starch. Pale shades for two browns would be made by thickening with gum water instead of starch.

No. 136. Koechlin's Brown, 1851.

1½ gallon water—1 pint acetic acid—2¾ lb. catechu—boil, and add 3½ lb. salammoniac—1½ lb. acetate of lime liquor, and while hot dissolve in 2½ lb. gum Senegal, and when cold add 9½ oz. nitrate of copper at 110° Tw.

No. 137. Resist for Catechu Colours.

4 gallons lime juice at 7°—1½ gallons of same at 45°—1½ gallons of tartrate of chromium—20 lb. dark British gum.

No. 138. Catechu Drab for Madder or Garancine.

The catechu drabs are generally made from browns, as for example, a standard may be prepared from say No. 126, by adding one measure of muriate of iron at 80° to 20 measures of the brown, and this standard reduced to shade required by either common gum water, or what is preferable, a prepared gum water, containing a certain proportion of salammoniac and salt of copper; the standard being strong, a medium shade might be obtained by taking 1 measure of and 6 measures of the reducing gum water. I give a few other receipts differently made up or with some differences in material.

No. 139. Catechu Drab for Dyeing.

7¼ gallon of a catechu liquor made from 30 lb. of catechu, 10 gallons water and 2½ gallons vinegar—add 1 quart acetic acid—2½ gallons water—6 oz. acetate of copper crystals—2 oz. sulphate of iron—4½ oz. alum—12 lb. gum. It is generally believed that muriate of iron is the only reliable iron salt for using with catechu drab.

No. 140. Catechu Drab for Dyeing.

7½ gallons water—25 lb. salammoniac—25 lb. catechu—boil, cool, and add 2½ gallons of acetic acid—1¼ gallons of acetate of copper made by dissolving 4 lb. sulphate of copper and 2 lb. acetate of lead in one gallon of water. This forms

the standard from which various shades are made by reducing with gum water and adding muriate of iron, usually taking 1 part of muriate of iron at 10° to 5 parts of the standard, and gum water from 2 to 12 parts for 5 of the standard; a greater quantity of muriate of iron may sometimes be used for darker shades.

No. 141. Catechu Drab for Dyeing.—*Penney.*

Standard made with 4 gallons water—12 lb. catechu—12 lb. salammoniac—6 pints acetic acid. Take 2 gallons of the standard—4½ gallons gum water—2 quarts of muriate of iron at 14°—1 quart of the fixing liquor, No. 131.

No. 142. Catechu for Chroming.—*Spirk.*

1 gallon water—6 oz. alum—3 pints wood acid at 3°—3 lb. catechu—2¾ lb. gum.

No. 143. Alkaline Catechu for Chroming.—*Spirk.*

1½ lb. catechu—1¼ gallon water—2 lb. flour—boil, and add 14 oz. caustic soda at 66° and 1 quart of water.

No. 144. Padding Shade for Chroming.—*Spirk.*

1½ gallon calcined farina—1 quart catechu liquor at 14°—1 pint berry liquor at 8°—1½ oz. logwood liquor at 14°.

No. 145. Steam Catechu Brown; dark.—*Spirk.*

1¾ gallons red wood at 3°—1 quart acetic acid at 8°—2½ lb. catechu—½ lb. salammoniac—7 oz. crystals acetate of copper—10 lb. gum Senegal. This and similar colours are employed in conjunction with wood colours to make an imitation of dyed garancine work.

[*To be continued.*]

7. *Action of Nitrous Acid upon Alizarine Colours.*

THE phenomena of the action of nitrous acid gas upon madder or alizarine colours mentioned in the "Textile Colourist," Vol. i., p. 79, as observed by M. Strobel, has been

further investigated and reported upon by M. Rosenstiehl. As our friends in Mulhouse appear to treat the observation of M. Strobel as a new one, it may be as well to mention that the fact has been published previously, as may be seen from the following extract from the Editor's "Chemistry of Calico Printing," p. 56, which appeared in 1860; the same appeared in the "Dictionary of Calico Printing," p. 161, which was published in 1862.

"Bioxide of Nitrogen, called also Nitric Oxide, Nitrous Acid, and Deutoxide of Nitrogen. . . . No applications; but is, I think, capable of receiving some. . . . Acting under the impression that the oxymuriate of tin used for cutting or altering the shade of madder reds produced its effects by some nitrous acid or hyponitrous contained in it, I tried the effect of the bioxide of nitrogen mixed with air upon strips of madder red previously damped. The action of the gas was prompt and energetic, the whole colour was changed to a yellowish shade, upon soaping it developed into a fine pink. If the gas was too strong, or the fents left in too long, the change to yellow became permanent, and soaping only developed a cinnamon shade, which appeared to be quite as stable as other madder colours, resisting the action of soap, acids, and chloride of lime."

At the date of this observation, about 1857, the Editor prepared a solution of tin charged with nitrous acid, had it thickened and printed by block upon madder reds, and so obtained yellow or orange effects, but the process had no practical value, and was not carried out.

Since the publication in the Bulletin of the Industrial Society of Mulhouse of Mr. Strobel's observation, a letter has been received by M. Schaeffer from Mr. Steiner, of Ribeauvillé, stating that in 1872 he had made an application of the action of nitrous acid upon madder reds dyed upon oiled cloth, M. Steiner writes:—

"Having to produce a design which required a flesh colour upon a ground composed of three shades of red, I tried to make this shade out of the ground colour by acting upon it with nitric acid and its derivatives. For this purpose I printed upon the pink and second red a colour composed of nitrate of lead and tartaric acid, and dried rapidly at a

temperature of 140° F. After washing, the pink was found changed into a fine flesh colour, and the second red into orange. These shades were not changed by the discharging vat, nor by passing in neutral chrome."

M. Rosenstiehl observes with regard to this letter that the process of M. Steiner having been kept secret and not published until now can have had no influence upon the discovery of orange alizarine, and does not in any way diminish the value of M. Strobel's observations. We may say that though it is a small matter to have observed a phenomenon, and it is well to be exact in small matters, still the chief credit must be given to those who like M. Rosenstiehl investigate phenomena and explain them.

M. Rosenstiehl's paper upon nitrated alizarine is in the Bulletin of the Industrial Society of Mulhouse last to hand, p. 247, and from it we extract what follows:—

The rough product of the action of nitrous vapours upon alizarine is a mixture which after being washed with water is formed of two colouring matters, one of which dyes alumina mordants red and the other orange. The first is unchanged alizarine, which can be separated by various methods. I have employed with advantage a slight excess of caustic soda which dissolves the alizarine, and acts but slightly upon the orange colour, the alkaline compound of which is insoluble in excess of soda.

The soda salt, after several crystallizations from water, is decomposed by an acid, and the colouring matter set at liberty. It is purified by a series of crystallizations from chloroform until it is found that the crystals and the mother liquor give the same shades by dyeing. The pure product dried in a vacuum at 212° F., gave by analysis numbers which correspond to the composition of mononitrated alizarine.

$C_{14} H_7 (NO_2) O_4$	Found.	Calculated.
Carbon	58·87.....	58·94
Hydrogen	2·56.....	2·45
Nitrogen	4·87.....	4·91

The author expresses his obligations to M. Goppelsroeder for his aid given in the analysis.

Nitroalizarine crystallizes from chloroform, which appears to be its best solvent, in the form of orange plates with a green reflection ; it is slightly soluble in warm water, which becomes coloured ; it is soluble in different neutral solvents and in acetic and sulphuric acid.

It can be sublimed, but is in great part destroyed by the operation, but it yields yellow plates with a greenish reflection and red needles. In dyes with distilled water, the addition of one equivalent of acetate of lime slightly improves it ; the bicarbonate of lime precipitates it completely. The precipitation is retarded by the presence of carbonic acid, which, however, cannot decompose the lime lake already formed. Its behaviour, therefore, is different from alizarine, and more resembles purpurine, which, like it, is a ter-substitute of anthraquinon ; the combinations it forms with bases are more stable than those formed by purpurine.

The resistance of the lime lake to the action of carbonic acid permits the presence of alizarine to be detected if it exists in the nitro-derivative. For this purpose I prepare a dye bath with sufficient bicarbonate of lime to precipitate both colouring matters and raise it to the boil ; the carbonic acid is expelled and the lime lakes form ; the complete precipitation can be ascertained by testing with bits of mordanted calico, which ought not to be in the least coloured. I then pass a current of carbonic acid into the mixture, which sets the alizarine free, which is easily proved by the colours communicated to mordanted calico by this principle.

Nitrated alizarine dyes iron mordants of a colour near to that designated three-violet, $\frac{3}{10}$ black on Chevreul's scale, and alimuna mordants of the colour of four-red-orange. The last colour is tolerably brilliant, and is improved by soaping.

The nitrated bodies are readily transformed into amines by proper reducing agents, and I thought it desirable to experiment upon the nitroalizarine by treating the alkaline solution with phosphorous. The colour gradually changed from violet to blue, green, and finally became yellow.

If the reduction be stopped at the point when the liquid is blue, a substance can be isolated which dyes alumina

mordants a chocolate colour; when the reduction is wholly accomplished a substance is obtained which dyes the alumina mordant a catechu brown shade. I have not prosecuted my researches further in this direction.

Of the nitrated compounds which act as colouring matters, such as picric acid, nitroalizarine is the only one yet known which unites with mordanted vegetable fibre, and from the colour which it yields being fast and bright, it will probably receive some useful applications.

[In a note it is stated that a German manufactory has sent out a product under the name of "alizarine orange," which is actually nitroalizarine that this establishment has succeeded in producing in a practical manner.]

8. *British and Foreign Patents, from the Commissioners of Patents Journal, May 26th to June 23rd, 1876, inclusive.*

Bleaching, Dyeing, Steaming, Washing, Engraving.

275. ANTHONY GAPPER SOUTHEY, of 3, New Inn, Strand, in the county of Middlesex, Civil Engineer, has given notice to proceed in respect of the invention of "Improvements in the mode of and apparatus for recovering the alkali from waste leys used in boiling vegetable fibres, and in utilizing the products obtained thereby.
2529. JOSEPH JULIUS SACHS, of Canada Government Building, King Street, Westminster, in the county of Middlesex, Manufacturer, for an invention of "Improvements in bleaching and preparing for dyeing or printing cotton, wool, hemp, flax, jute, and other fibrous materials."—Dated 19th June, 1876.
1174. WILLIAM MATHER, of the firm of Messieurs Mather and Platt, of Salford, in the county of Lancaster, Engineer, for an invention of "Improvements in apparatus for steaming and ageing printed fabrics."—Dated 18th March, 1876.—This patent has passed the great seal.
2277. THOMAS EVANS and WILLIAM DEAYMAN, of Walsall, in the county of Stafford, Manufacturers, for an invention of "Improvements in apparatus for washing textile fabrics."—A communica-

tion to him from abroad by Josiah Brown, of Monticello, county of Sullivan, New York, in the United States of America.—Dated 30th May, 1876.—Provisional protection has been granted.

364. THOMAS NIXON, Pentagraph Engraver to Messrs. John Orr Ewing and Company, of Alexandria, in the county of Dumbar-ton, North Britain, has given notice to proceed in respect of the invention of "Improvements in pentagraph engraving machines.

Printing, Dyeing, Colouring Matters.

2268. WILLIAM BROOKES, of 62, Chancery Lane, in the county of Middlesex, Patent and Registration Agent, for an invention of "Improvements in printing in colors upon paper or other fabric or material and in the apparatus employed therein."—A communication to him from abroad by Carl Heinrich Otto Radde, of Hamburg, in the empire of Germany, Merchant.—Dated 30th May, 1876.—Notice to proceed has been given.
2048. JOE FROST of Huddersfield, in the county of York, Chemist, and JOHN WALMSLEY, of Mirfield, in the same county, Printer, for the invention of "Improved means or methods of obtaining two or more colours on piled fabrics or on material intended for such fabrics with a view to imitate the skins of animals or produce designs thereon, such means being also applicable to produce different effects on natural skins or furs."—Provisional protection has been granted.
670. JOSEPH FIRTH, of Leeds, in the county of York, has given notice to proceed in respect of the invention of "Improved apparatus for use in dyeing fabrics indigo blue."
2534. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for an invention of "An improved black dye."—A communication to him from abroad by Charles Rave of Paris, France.—Dated 19th June, 1876.
1851. RICHARD SIMPSON, ARTHUR BROOKE, and THOMAS ROYLE, all of Greenford Green, Alizarine Works, Harrow, in the county of Middlesex, have given notice to proceed in respect of the invention of "Improvements in the preparation of alizarine and other analogous colouring matters made from anthracine."

Yarns, Hanks, Cops.

468. CHARLES TOUSSAINT, one of the firm of Toussaint, Levy, and Co., of Saint Dié, in the department of the Vosges, France,

Manufacturer, have given notice to proceed in respect of the invention of "Improvements in bleaching cotton on shuttle cops, bobbins, or in hanks."

4301. M. BAERLEIN, of Manchester, for "Mordants, dyes, and sizes for yarn."—5 years.—Dated 19th January, 1876.—Saxon patent.

Wool Treatments.

944. GEORGE RYDILL, of Grove House, Dewsbury, in the county of York, for an invention of "Improvements in utilizing waste heat in drying wool, hair, woollen and linsey rags, woollen piece goods, chemically treated with acids for removing vegetable substances therefrom."—Dated 4th March, 1876.—This patent has passed the great seal.

2016. HENRY EDWARD NEWTON, of the Office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, for the invention of "An improved process and apparatus for removing pieces of straw, wood, and other vegetable substances from fabrics made of wool, silk, hair, or other animal fibres."—A communication to him from abroad by François Delamare, the younger, of Paris, in the republic of France.—Provisional protection has been granted.

2018. ALBERT HOPFF, Merchant, of Hamburg, for the invention of "Improvements in apparatus for removing burrs out of wool."—A communication to him from Carl Ulbrich, a person resident at Chemnitz, in the kingdom of Saxony.—Provisional protection has been granted.

2139. ISAAC BLUE HARRIS, of Castle Mills, Fountainbridge, Edinburgh, has given notice to proceed in respect of the invention of "Improvements in wringing rollers for wool-washing and similar machines."

2294. WILLIAM PHILLIPS THOMPSON, of the Office for Patents, 6, Lord Street, Liverpool, in the county of Lancaster, Consulting Engineer, for an invention of "Improvements in apparatus for washing wool and other similar fibre."—A communication to him from abroad by Frederick G. Sargent, of Graniteville, Middlesex county, Massachusetts.—Dated 31st May, 1876.—Provisional protection has been granted.

2477. SAMUEL BAMFORD, of Royton, in the county of Lancaster, for an invention of "Improvements in the method of treating mixed woollen fabrics for the purpose of separating the wool

from any other fibrous material employed in the manufacture of such fabric."—Dated 15th June, 1876.—Provisional protection has been granted.

- 2505.—EDWARD GRIFFITH BREWER, of Chancery Lane, London, for an invention of "Improvements in bleaching and purifying wool."—A communication to him from abroad by Messrs. Daudier, père et fils, of Paris, France.—Dated 16th June, 1876.
- 39,425. J. M. DICK, for an imported invention of "A process and apparatus for removing moisture from wool and other similar substances."—Dated 24th April, 1876.—(French Patent, 24th April, 1876.)—Belgian patent.

Finishing Processes.

1904. ARTHUR BARRACLOUGH, of Boy's Mill, Halifax, in the county of York, Woollen Manufacturer, for an invention of "Improvements in apparatus for dewing, damping, and oiling fabrics and fibrous materials."—Dated 27th May, 1873.—This patent has become void.
1911. JONATHAN TINDAL, of the firm of Tindal, Son, and Company, Cloth Finishers, both of the city of Glasgow, in the county of Lanark, North Britain, for an invention of "Improvements in finishing cloth, and in machinery or apparatus employed therefor."—Dated 18th May, 1873.—This patent has become void.
269. OATES, INGHAM, of the firm of Oates, Ingham, and Sons, of Bradford, in the county of York, Dyers and Finishers, and CHARLES HERBERT HOLT, of Huddersfield, in the same county, Engineer, have given notice to proceed in respect of the invention of "A new or improved method of, and apparatus for, steaming or 'blowing' woven fabrics in the process of dyeing and finishing."
242. GEORGE HENRY NUSSEY and WILLIAM BRADSHAW LEACHMAN, both of Leeds, in the County of York, have given notice to proceed in respect of the invention of "Improvements in machinery or apparatus for pressing woollen and other woven or felted fabrics."
498. ANDREW MITCHELL TORRANCE, of the firm of Miller, Son, and Torrance, of Cannon Street, in the City of London, for an invention of "Improvements in the numerical marking of piece goods and other materials and fabrics sold by length, and in apparatus therefor."—Dated 8th February, 1876.—This patent has passed the great seal.

1845. JOSEPH HOWARTH, of Rochdale Road, Manchester, in the county of Lancaster, Plumber and Glazier, for an invention of "Improvements in apparatus for heating the cylinders of machines for calendering, mangling, and drying."—Dated 2nd May, 1876.

1987. HENRY EDWARD NEWTON, of the Office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, for an invention of "Improved apparatus for applying starch or other analogous preparations to various articles made of textile substances."—A communication to him from abroad by Thomas Shirès Wiles and Alonzo Pelton Adams, both of Albany, in the state of New York, United States of America.—Dated 11th May, 1876.—Provisional protection has been granted.

173,398 ALBERT J. ELWELL, of Woonsocket, assignor to the Lippitt Woolen Company, of Providence, R.I., for "Machines for surface-finishing woolen fabrics."—Application filed 4th November, 1875.—American patent.

Brief.—"Instead of the common 'rubber,' a brush is employed, to which a small rapid rotary motion is given. A revolving cylindrical brush is employed to remove from the back the rolls, &c., occasioned by the action of the above-named device."

Claim.—"1, the improvement in the art of surface-finishing chinchillas, beavers, and other similar heavy woolen fabrics, which consists in developing the tufts or knots of fiber on the surface, by subjecting said surface to the action of a reciprocating brush, operating substantially in the manner described. 2, in a machine for finishing the front surface of heavy woolen goods, the combination, with a platform for sustaining the fabrics, of a brush and mechanism for imparting thereto a vibratory longitudinal and lateral motion in a plane parallel with the platform, substantially as described. 3, in a machine for finishing the front surface of heavy woolen fabrics, the combination, with a platform for sustaining the fabrics, and feeding and conducting rolls for passing the fabric along the platform, of a reciprocating brush arranged to operate on the front surface of the fabric, substantially as described. 4, the combination, in a chinchilla or petesham finishing machine, with the platform and the reciprocating surface-finishing device, of a rear surface-brush, substantially as described, for the purpose of removing the rolls or tufts of fiber developed on the rear surface of the fabric by reason of its movement on the platform, incident to the action of the rubber or other reciprocating finishing device, as set forth."

39,405. H. LUTASTER-CROISIER, for "An apparatus for glazing chintz."—Dated 25th April, 1876.—Belgian patent.

THE TEXTILE COLOURIST.

No. 8.]

AUGUST, 1876.

[Vol. II.]

1. *Progrès de l'Industrie des Matières Colorantes Artificielles*, par A. Wurtz, Membre de l'Institut. (*Progress of the Manufacture of Artificial Colouring Matters*, by A. Wurtz. Paris, G. Masson, 1876.)

THIS work, by one of the leading chemists of France, is a portion of the jury reports upon the Universal Exhibition held at Vienna, in 1873. It gives an account of such new products as have made their appearance since the Paris exhibition of 1867, as well as of improvements in the manufacture of colouring matters then known. The reputation of the author as a chemist, and the assistance which he has received from other chemists and manufacturers, of whom he especially mentions M. Charles Girard, give to this little treatise a stamp of authority which will make it very welcome to students of colour chemistry, as fixing the exact state of the progress of discovery in artificial colouring matters in the year 1873. It does not purport to be a complete treatise upon the artificial colouring matters, but to take up the subject where it was left by the reporters of the international jury of the exhibition of 1867, and as little as possible is said of the processes then known and practised; it does not therefore supersede, but rather supplements the several excellent treatises upon the tar products, which are well known to those interested in this branch of industry.

The primary material, coal tar, was formerly obtained exclusively from gas works, but is now also largely produced and saved in the process of coke making, owing to the inven-

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tions of Messrs. Powell, Dubochet and Knab. The coke-ovens mostly employed are the so-called Belgian ovens, of which twenty are connected together, the gas evolved being used to heat the ovens. The coke produced is said to be of excellent quality. England is by far the largest producer of coal tar, which, since the discovery of the aniline colours, brings from nine to ten times the price it was previously sold for. The Paris gas company have succeeded of late years in producing a liquid tar, very rich in light oils, by a process which does not appear previously to have been made public. The method of extraction is due to MM. Pelouze and Andouin. The tar in impure gas is in the form of a yellow cloud, which is made up of excessively fine drops or bubbles. When a jet of such gas is made to impinge on a sheet of paper, the drops or bubbles burst and deposit on the paper a dark stain of tar. Upon this phenomenon the inventors founded their ingenious process for removing the last particles of tar from gas. The gas is caused to pass through fine holes drilled in a brass plate, and the jets strike against another plate placed at a short distance, which is also pierced with an equal number of holes. But as these holes do not correspond in position with those in the first plate, the small jets of gas strike against the metal, and so effect the flattening or bursting of the tar globules or bubbles. After traversing the holes of the second plate, the gas jets again strike the plain parts of a third plate similarly drilled with holes. These two contacts are sufficient to deprive gas of its tarry particles, and a jet thus purified does not soil white paper. As this passage through fine openings causes a loss of pressure, it is found necessary to exhaust the gas from the first condensers, where it is cooled, and by means of pumps obtain sufficient pressure to make it pass freely through the plates, whence it passes into the usual purifiers, and in which it is found, that being freed from so much tar, it requires less pressure than in the ordinary purifying systems. At one of the gas works where this plan is at work, from a daily production of 80,000 cubic metres of gas, there is obtained 600 litres of a very rich tar which yields 20 per cent. of light oils, while the common gas tar gives only from 3 to 5 per cent.

In the distillation of tar some changes have taken place, owing to the demand for anthracene. Formerly the pitch left contained a considerable portion of the heavy oils, but to obtain the anthracene oils it is necessary to push the distillation almost to its utmost limits, say to 350° or 400° Centigrade, which leaves a brittle, dry, pitch. The anthracene oils are those which come over last, they are of a buttery consistence and greenish colour.

There does not appear to be any novelty in the treatment of the light or medium oils, or the method of purifying them. All those oils which distil at a temperature below 120° C. are generally called benzoles, and their commercial value is estimated from the proportion which distils over at a temperature not higher than 100° C.; thus there are benzoles of 90 per cent., 60, 30, and 20 per cent. A benzole of 90 per cent. yields an aniline suitable for blue and black; a benzoline of 30 to 40 per cent. gives a good aniline for red. For the latter colour it is not only useful but actually necessary to have a mixture of benzine and toluine, for it is known from the researches of Hoffmann that rosaniline contains the diatomic radical toluylene, which comes from toluine. However, there must not be too much toluine in the benzol; a benzole of only 20 per cent. is bad, for it yields an aniline which is too heavy.

In the separation of light oils improvements have been made in distilling and condensing apparatus, by means of which the various hydrocarbons can be obtained in a pure state. The principle employed is old, and long since used in distilling alcoholic liquors, but the difficulties of adopting it to these fluids were first practically surmounted by M. Coupier. The vapours from the mixed hydrocarbons are made to pass over trays of solution of chloride of calcium, which can be kept at required temperatures by coils of steam piping or other contrivance. Suppose a mixture containing benzine boiling at 80° C. and toluine boiling at 108° is distilled, the chloride of calcium bath is heated to 80° C., this does not permit the condensation of the vapours of benzine, which pass on in the state of vapour while the toluine

is condensed the benzine passes on and is condensed and collected further on. In a graphic representation of the products obtained, M. Coupier shews that out of 100 litres of light oils he obtained

Impure mixtures boiling between	62° and 80°	6 litres.
Pure benzine	80	44
Impure mixtures	82	6
Pure oil	110	17
Impure mixtures	112	5
Pure oil	137	9
Impure mixtures	140	5
Pure oil	148	8

To separate the oils of high boiling point, as xylene, the chloride of calcium is replaced by a saturated solution of nitrate of ammonia, or by paraffin, which are heated by superheated steam.

The sections upon the treatment of the heavy oils, the extraction of phenol, or carbolic acid, preparation of naphthaline and anthracene do not present any novelties.

The only improvement recorded in the preparation of nitrobenzole consists in certain modifications of apparatus by which the nitrous gases evolved are condensed in coke towers. It is preferred to mix the nitric acid and benzole in cylindrical boilers, placed horizontally, and not vertically as formerly, they are quite closed and in connection with condensing vessels and the coke tower. Three hundred kilos. of benzine can be acted upon at once, and there need be no offensive exhalation of nitrous gases at any stage of the process.

In the preparation of aniline a modification has been introduced; the reduction of the nitrobenzine by iron and acetic acid being accomplished, instead of distilling the whole mass, the greater part of the aniline formed is separated by decantation by means of taps. The acetate of aniline thus obtained is treated with soda; the aniline separated and rectified is ready for sale. The aniline which is not decanted off is distilled over by means of a current of steam, and thus a considerable saving in fuel is effected.

The toluidines are prepared in the same way as aniline, and the pseudotoluidine separated by a second operation, which consists in incompletely saturating the mixture with sulphuric acid, and distilling by means of a current of steam, the toluidine combining preferably with the acid remains in the still as sulphate, while the pseudotoluidine distils over; a second fractional saturation and distillation yields pure pseudotoluidine. The sulphate remaining being decomposed by an alkali furnishes solid toluidine, which serves to prepare ditoluyllamine (decrysylamine) which yields a blue colouring matter when treated by chloride of carbon in presence of diphenylamine, but if the pseudotoluidine be not previously separated the colour is not pure, for this substance, under the same circumstances, gives a mahogany colour.

The description of the preparation of fuchsine, magenta, or the hydrochlorate of rosaniline, by means of arsenic acid, does not present any novel features. The Coupier process without arsenic consists in heating in an enamelled iron pan the following proportion of materials:—

Aniline for red, containing toluidine	38 parts
Nitrobenzine	17 to 20 „
Hydrochloric acid	18 to 22 „
Cast-iron turnings	2 „

The whole is heated to about 180° C. for five hours, when it becomes thick; it is then taken out and cooled in iron trays. The "melt" or crude matter contains about 25 per cent. of aniline, which is recovered by carefully saturating with lime, and distilling, and the magenta is obtained from the residue in the usual manner.

Coupier's blue is prepared by pushing the heating of the above mixture to a higher degree and for a longer time. The crude product is heated with five times its weight of sulphuric acid for four hours in iron vessels, commencing at a temperature of 50° C. and finishing at 90° . Twelve kilos. of the crude melt give about 60 kilos. of the sulpho-conjugate acid, which is precipitated by adding 400 kilos. of water. The blue precipitate is collected upon filters and washed with water. It is

employed for printing blacks and greys. The blue is dissolved in caustic soda, dried, and sold in the form of small dry pieces of a black-blue colour, which dissolve in water with a rich blue colour. The specimens of this colour upon woollens shew a dark blue-black and a bluish grey, such as would be formerly obtained from galls and iron.

In describing the rosaniline blues called *bleu de Lyon* and the soluble blues, M. Wurtz had the advantage of the assistance of M. Poirrier, one of the most important makers of these colours, and was permitted by that gentleman to visit his manufactory and follow out the processes in detail.

The operation is conducted in boilers of a capacity of 250 litres provided with an agitator, and heated in a bath of oil. Twenty kilos. of crystallized rosaniline are introduced, and from 4 to 8 kilos. of aniline, according to the shade of colour required, and about 10 per cent. of crystallized benzoic acid added. The whole is heated to 180° C. According to the proportion of aniline employed, the blue is more or less of a reddish shade, there being three well-defined compounds—the monophenylated rosaniline being reddish, the diphenylated less red, and called blue, and the triphenylated, called blue-blue. To judge of the progress of the operation, a workman takes out a sample from time to time and places it upon a plate beside a sample of the right colour. Alcohol is then dropped upon each sample, and, the plate being inclined, the colours of the solution can be easily compared.

When the operation is terminated, the mass must be quickly cooled. The boiler is lifted from the oil bath by a crane and placed on a platform over or near to a vat which is to receive its contents. The thick mass is expelled by pressure of air from a condenser, and received into the vat, where it is agitated with dilute hydrochloric acid to remove the excess of aniline. The blue remaining insoluble is collected upon filters and washed. The blue is further purified by alcohol or benzine, which dissolves a certain quantity of red or violet matters.

The *bleu lumière*, or sky blue, is the result of a further purification of the above blue. The process of MM. Girard and

Laire consists in treating a good quality of blue with small quantities of hot alcohol, and then dissolving all up in boiling alcohol mixed with aniline. The liquor is filtered and lightly supersaturated with ammonia or, preferably, by an alcoholic solution of soda, a small portion of the blue precipitates carrying with it the impurities. After cooling, the precipitate is separated by filtration, and, by adding hydrochloric acid in excess, the purified blue is precipitated, the remaining impurities resting in the solution. This blue is insoluble in water, and can only be employed in alcoholic solution, which is very inconvenient in dyeing. It has, however, been made soluble by treatment with sulphuric acid, a process first indicated by Nicholson. There are four sulpho-conjugated compounds of this blue obtained by operating upon it at different temperatures with strong sulphuric acid. Nicholson's blue is the mono-sulphated compound. It is not soluble in water, but dissolves in alkali, losing its colour. The dyeing is performed in neutral liquors, and the blue developed by passing the goods in acid. The blues soluble in water contain more sulphuric acid than this one.

The various stages through which the manufacture of the methylaniline violets have passed are well described by M. Wurtz. As is well known, Hoffmann was the first to produce these colours by acting upon rosaniline with the iodides of methyl and ethyl. The high price of iodine, its limited supply, and the monopoly of it in the hands of a few persons, incited inventors to discover some other methods of producing these colours. The first real step in advance was the discovery by Bardy of an economical method of preparing methylaniline by heating under pressure a mixture of hydrochlorate of aniline and wood naphtha, by which he obtained hydrochlorate of methylaniline and water. To Lauth is due the completion of the process. He had made numerous experiments with the view of oxidizing methylaniline, and had found that the hydrochlorate of this base became violet by simple exposure to a warm atmosphere; and finally he fixed upon the chloride of copper, which had previously been used by Dale and Caro for a similar purpose, as a suitable oxidizing agent.

The practical operations commence by heating together in a strong autoclave a mixture of equal parts of wood naphtha, aniline, and hydrochloric acid by means of a bath of oil. The heat is pushed as high as 200° or 220° C., and a pressure of twenty-five atmospheres is developed. When the action is complete, the mass is cooled, and the base separated by a slight excess of lime; it is then distilled in a current of steam. The chief product is dimethylaniline, which may form from 80 to 95 per cent. of the mass, besides which, there is present monomethylaniline and some uncombined aniline with other products, which are separated by various means.

The methylaniline is treated as follows :—Upon a stone bed the materials below are mixed with a spade.

Sand	100 parts.
Methylaniline	10 „
Nitrate of copper	3 „
Common salt	2 „
Nitric acid	1 „

The sand is placed so as to have a cavity in its middle, into which the methylaniline and other products are placed. The oxidation commences immediately, and during the mixing the mass becomes heated and coloured. After a certain time the dark-coloured mass is made into large blocks by pressing in wooden frames, and carried to a stove heated to 40° C., where they remain twenty-four hours; at the end of this time the blocks have become hard, and acquired a beautiful cantharidine-green colour. The colouring matter is combined with copper salt, and has to be separated from it. To effect this the blocks are ground in a mill to powder, mixed with water, and treated with a solution of sulphuret of sodium of known strength; the copper is transformed into sulphuret, and the colouring matter set at liberty, but it remains insoluble mixed with sand and the sulphuret of copper. The whole is drained and twice washed, and then the colouring matter is dissolved out, first by boiling water and lastly by water slightly acidulated with hydrochloric acid. The addition of common salt precipitates the colouring matter as a soft mass, which is collected together by a spade, dried, ground, and sent out for

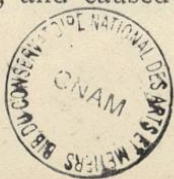
use by the dyers. This process yields a pure shade of violet. To obtain redder shades it is necessary to have a larger proportion of monomethylaniline in the first instance; but the reddest shades cannot be obtained except by the direct methylation of rosaniline by Hoffmann's process.

The so-called aldehyde green was the first artificial green colouring matter discovered. It is no longer manufactured, having been displaced by the iodine green, which, according to the researches of Hoffmann and Girard, is the dimethyliodhydrate of trimethylaniline. The best method of its manufacture is the following. In a strong enamelled iron autoclave provided with an agitator, there is placed

Acetate of rosaniline	10 kilos.
Methylaniline violet	20 „
Methylic alcohol	20 „

The mixture is heated for three or four hours by means of an oil bath. At the commencement the temperature may be raised to 120° C. without inconvenience, but towards the end it should not exceed 60°. The pressure rises as high as ten or twelve atmospheres. When the operation is completed, and the free gases liberated are condensed by being made to pass through a cooled worm, the mass in the autoclave is then heated in a water bath to 50° so as to distil off the iodide of methyl; after which it is dissolved in water at 60°, mixed and exactly saturated with carbonate of soda, and the excess of violet coloured matter is precipitated by a small quantity of common salt, the green colour remains in solution, and is separated from the precipitate by filtration, and then itself precipitated by picric acid. The combination thus obtained is so little soluble in water that it has to be dissolved in weak alcohol for dyeing, an inconvenience which MM. Laire and Girard overcame by using sulphate of zinc instead of picric acid. The zinc compound produced is crystallizable, and very soluble in water.

The green from the methylaniline violet called "vert lumière," or light green, is prepared quite in another manner, and by the assistance of the nitrate of methyl, a substance which is very explosive, and caused many serious accidents



until its properties were better understood. The following proportions are taken:—

Violet de Paris	2 parts
Methyl alcohol	3 „
Nitrate of methyl.....	1 „
Lime sufficient to saturate the acid in the Violet de Paris.	

These materials are introduced into a large cast-iron cylinder, upon an axis, placed horizontally in a water bath for half its depth. It is heated for ten or twelve hours with continual agitation. When the operation is completed, the contents of the cylinder are emptied into a vat of water by being forced out of the interior by pressure of condensed air; hydrochloric acid is added to neutralization, and then the whole is boiled. The excess of violet is precipitated by addition of common salt and filtration. A further purification is effected by cautious fractional precipitation with chloride of zinc and filtration. Finally an excess of chloride of zinc is added, and the product purified by crystallization.

The use of nitrate of methyl involving risk of explosion, attempts have been made, and it is said with success, to employ instead the chloride of methyl. This substance being a gas at ordinary temperatures, and when liquefied boiling at 12° C. below zero presented great difficulties; but these have been overcome by M. Monnet, of Plaine, near Geneva. The chloride, prepared in special apparatus, is kept in strong reservoirs, with an indicator to shew its level, and by proper communications a proper quantity is allowed to distil over into cooled autoclaves containing an alcoholic solution of the violet base, and the mixture heated to 80° C. The resulting product is the dichloromethylate of trimethylated rosaniline.

The author has nothing to say upon aniline black which would be new to our readers.

The colouring matter, safranine, was first indicated by M. Willm, and practically manufactured by Mr. Perkin. It has to some extent replaced safflower in dyeing. The bases used

are preferably those which are distilled over in the preparation of magenta, and they consist of aniline and pseudotoluidine, the crystallizable toluidine which appears to be unfitted for the production of this colour being retained by the mixture in the still. M. Poirrier's process of manufacture is as follows:—In large cylinders of enamelled cast-iron placed in cold water the above mixture of bases is introduced along with nitrite of potash prepared by the action of heat upon nitre. Hydrochloric acid is added in small quantities, with constant agitation, so as to prevent as much as possible the evolution of nitrogen, which would be caused by too rapid action. The result of this action is then placed in a vessel in a water bath, and a further quantity of the mixed bases, and the whole is oxidized by heating with arsenic acid. When a portion taken out dissolves in alcohol, with a violet-red shade, the whole is transferred to a wooden vat filled with water and boiled up by steam, and then filtered. The clear solution is then boiled with bichromate of potash to complete the oxidation which, in the action of the arsenic acid, was purposely left incomplete. When the red colour is fully developed, milk of lime is added in quantity sufficient to neutralize the excess of acid. A precipitate of arseniate of lime is formed, mixed with arsenite of lime and oxide of chromium, which has a black colour, owing to the presence of aniline black or grey. The liquor is filtered, and the safranine precipitated by common salt.

In other establishments modifications of this process are employed for the purpose of treating the bases with nitrous acid, in some cases the gas itself being employed, in others nitrite of lead.

The diphenylamine blues have made their appearance since 1867. The base itself was discovered in 1864, but it was not employed in colour-making until some years afterwards, when MM. de Laire, Chapoteaut, and Ch. Girard prepared it by heating under pressure a mixture of aniline and hydrochlorate of aniline at a temperature of 250° C. for twenty-four hours. In the first experiments the yield was only 25 per cent. of the weight of aniline employed, but by discharging the ammonia gas formed from time to time, double that amount was even-

tually obtained. The resulting mass is treated with concentrated hydrochloric acid to form hydrochlorates of the bases diphenylamine and aniline, and then, by addition of a considerable quantity of water, the first salt is decomposed, and the base floats on the water, and solidifies on cooling. It is purified by washing, pressing, and distilling. The next step is to combine it with the elements of sulphuric acid by heating it strongly with the concentrated acid, and, after purification, there is obtained a conjugate sulpho-compound, which becomes blue by oxidation. The method of preparing this blue, given by M. Wurtz, is by heating in an enamelled iron vessel, at a temperature not exceeding 130° C., one part of the sulpho-compound and two parts of ordinary oxalic acid for a space of eighteen or twenty hours. The resulting mass is boiled with water neutralized with ammonia, filtered, and the colouring matter precipitated by sulphuric acid. It is washed and combined with either ammonia, soda, or lime, dried, pulverized, and sent for consumption. The ammoniacal compound is used in silk dyeing, the soda compound for wool, and the lime compound for cotton.

In the articles upon picric acid, rosolic acid, aurine, and some others, we do not find anything of special interest. Upon the composition of aurine the author gives an account of the experiments of Messrs. Dale and Schorlemmer, in which they determined its true composition.

In the naphthylamine series the only interesting product is a pink colour called rosanaphthylamine, used in silk dyeing.

Upon alizarine from anthracene so much has been recently published in England that it is easy to place one's self in advance of the contents of this work. The specimens of colour dyed with alizarine are rather unfortunate, and give a very low idea of the value of this remarkable body.

M. Wurtz was censured not long ago for somewhat pompously announcing in an important work that chemistry was a French science. He may probably still think it was so at its modern birth, but in his concluding remarks, which we translate, it is interesting to find that he can give credit to other nations for their efforts and success in chemistry.

"The great scientific and industrial movement which is a characteristic of the present age is owing to the special direction and continued efforts of human intelligence in all civilized countries, and the results gained are the common property and common riches of all mankind. Each nation has its proper place in the great family. Each one has its history in the past and its future before it. It is, therefore, useful and proper to examine and define the part which each one has taken in the great movement which is changing the face of the globe. In time to come, the records of science and manufactures will occupy a place in general history not less prominent than those of politics and wars.

"At the commencement of the present century France was in excellent training for industrial discoveries. A constellation of illustrious scientists was at work in the laboratories, and chemical arts reaped the fruit of the great scientific reformation accomplished by Lavoisier and his pupils. Amongst the things completed it is sufficient to recall the discovery of artificial soda, by Leblanc, which has had so great an influence upon the progress of industry. But towards the middle of this century the scientific movement had visibly slackened its pace; men dwelt with pleasure upon the glories of the past, and adhered to its traditions. The new ideas which had arisen in science, and which have since given it a new life, were received here with coldness, but were welcomed on the other side of the frontier. The instruments of science, the formation and endowment of laboratories, with few exceptions, were just in the same state as at the commencement of the century. During this time neighbouring countries, Germany leading the way, had applied themselves to work. In all the important centres laboratories were erected, splendidly organised and richly endowed; nothing was wanting either to those who cultivated and taught science, or to those who desired to be its votaries. The latter came in numbers, and when they had acquired a solid knowledge spread themselves every year in the ranks of society, some as teachers, but the majority to devote their talents to industrial manufactures. Thus the laboratory is

at once a school of high science and a training ground for practical men.

"Let it not be thought that there is a great distance between theory and practice.

"This report will have been written in vain if it has not demonstrated clearly the important influence which pure science has had upon the discoveries of practice.

"If, unfortunately, the light of science should become dimmed, and some day extinguished, the practical arts will be devoted to rapid decay. The money which a state applies to scientific and superior instruction is a profitable investment, and Germany has quickly reaped the fruits of her foresight. Thirty or forty years ago manufactures there were hardly existing, to-day they are powerfully developed. The various manufactures which form the subject of this report furnish a striking example, although happily for us an exceptional one. From an approximative valuation which would appear to be not far from the truth, the value of the artificial colouring matters produced in the past year were :

In Germany.....	30,500,000 francs
	(of which 15,000,000 francs for alizarine)
In Switzerland.....	7,000,000 "
In England	9,000,000 "
In France.....	7,000,000 "

It is thus seen that this industry, which of all others is a scientific industry, has had a greater development in Germany than in all other countries together."

M. Wurtz then shews that the French have contributed largely to the discovery of artificial colouring matters, but that their commercial success has been injuriously influenced by the want of uniformity in the patent laws of the various European states. He continues :—

"In France anyone can obtain a patent for a new product, a new application of a known product, or a new process of making a known article. In England the patent law is nearly the same as in France. In the German Empire the patents are not valid unless certified by a commission of

examiners. In Switzerland there is no patent law, and no property in an invention. This state of affairs is a difficulty for French industry. Any stranger can patent his product or his process in France, while the French cannot profit by their patents in Germany except upon the condition of their being approved of by a commission of foreigners. In Switzerland they derive no advantage from their discoveries, have no privileges to protect them against the first comer who chooses to copy their patent in France, and work it on the other side of the frontier. It would be a great advantage to come to an agreement with foreign powers so as to regulate the property of discoveries in manufactures by international conventions, in the same way that literary property is now protected by international copyright."

We may notice, in conclusion, that this work is illustrated by five double-page plates, containing sixteen figures of apparatus, executed in a very superior style of lithography, and that there are twenty-nine specimens of dyed silk, wool, and cotton interspersed with the text, most of which are excellent illustrations of the colouring matters they refer to.

2. *Colouring Matters derived from Resorcine.**

BY M. LOUIS DURAND.

Preparation of Resorcine.—Benzine is acted upon by sulphuric acid, so as to substitute two equivalents of hydrogen by two equivalents of sulphuric acid; to effect this the benzine in vapour is passed into four times its weight of sulphuric acid heated to 464° F. The new compound remains dissolved in the excess of sulphuric acid, which is mixed with about ten times its bulk of water, and then saturated with lime. The sulphate of lime precipitates, and the bisulphobenzylate of lime remains in solution.

* *Moniteur Scientifique* (3), vi., p. 696.

The latter salt is now decomposed by addition of carbonate of soda, which is added as long as it produces a precipitate. The resulting products are carbonate of lime and bisulphobenzylate of soda. The solution is filtered, and the clear liquid evaporated to dryness in order to obtain the soda salt, which is white and like flour.

The next operation consists in transforming this salt into resorcine, a change which requires that the two equivalents of sulphuric acid should be removed, and replaced by two equivalents of hydroxyle. For this purpose it is necessary to treat the salt at a temperature of 480° with five times its weight of dry caustic soda. This is accomplished in cast-iron pans provided with mechanical agitators, and heated in a bath of oil. The operation lasts for twenty-four or thirty-six hours, and the materials have to be frequently tested, so that the heating may not be too long protracted, which would destroy the resorcine and give rise to a mass of complex substances entirely valueless.

The melted stuff, when finished, is poured upon cooled plates of cast-iron, and afterwards broken up into small pieces to facilitate its solution in water. The excess of alkali is neutralized by sulphuric acid, and the resulting sulphate of soda removed as much as possible by allowing it to crystallize out. The resorcine is left in solution. It is very soluble in water, and it is found best to extract it from the solution by agitating the whole with sulphuric ether, which removes it from the aqueous solution. The ethereal solution of resorcine is distilled to save the ether which leaves the resorcine in the retort, where, upon cooling, it forms a thick crystalline magma. The management of large quantities of ether required in some operations presents great difficulties, arising from its volatility and inflammability, and has already given rise to serious accidents.

Preparation of Phthalic Acid.—Naphthaline is acted upon by chlorate of potash and hydrochloric acid. Various chlorides of this base are produced, which are separated by treating the mixture with hot petroleum, which only dissolves that chloride capable of giving phthalic acid by oxidation.

Upon cooling, the petroleum deposits the chloride in crystals, which are collected and washed with the more volatile petroleum spirits to remove the solvent adhering to the crystals. The crystals are then treated with nitric acid until they are completely transformed into phthalic acid. This acid is purified by successive crystallizations. It is then dried by melting it in an oil bath, so as to expel all its water, for the succeeding operations require the phthalic acid to be anhydrous.

Preparation of Fluoresceine.—This consists simply in heating together, at a temperature of 383° to 392° F., 2 parts of resorcine and 1 part of phthalic acid. When the mixture has become very thick the operation is finished.

The crude melt is washed with boiling water to remove some products formed. The fluoresceine, being insoluble, is collected upon a filter and dried.

Fluoresceine, considered as a colouring matter, has no affinities for either vegetable or animal fibres. It does not dye silk either alone or with alkalis or acids. It forms lakes with metallic salts, the finest of which is that obtained from lead.

It is soluble in all proportions in alkalis. A few drops of an alkaline solution are capable of colouring vast quantities of water, and produce the strongest dichroism known. The mixture is yellow by transmitted light, and green by reflected. So powerful is this action that one part of the substance produces a visible effect on 45,000,000 parts of water. Fluoresceine was for a long time merely a chemical curiosity, until it was discovered that bromine combined with it, giving rise to the remarkable colouring substance which has received the name of eosine.

Eosine.—This colouring matter is a potash salt perfectly and largely soluble in water. It is coming into general use. The best fixing agent for it on cotton is lead. The calico is printed with a solution of eosine thickened with gum, steamed, and then fixed in acetate of lead. This gives more crimson or purple shades than when the colouring matter is fixed directly by albumen.

In silk dyeing it is found that the eosine soluble in water does not give very good results, the dark colours produced

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being detached by rubbing, which is an indication that a certain amount of the colouring matter is only in a loose state of mechanical combination. Preferable colours are obtained from a modification of eosine called *primrose*, and known also as alcoholic eosine.

Upon wool eosine gives cochineal-like shades, but its price is at present too high to allow it to compete with cochineal for dark colours. It may, however, be employed for light shades with advantage, since the cochineal colours lose much of their beauty when diluted. Wool dyes with it at 140° F., adding alum at the rate of 5 per cent. of the weight of the wool.

Eosine is used for making red ink. Fifteen grammes of eosine, soluble in water, with a little sugar and gum, gives a litre of good ink, better in shade than that made from carmine. It copies very well.

Primrose.—This modification of eosine is insoluble in water, but dissolves in weak alcohol. The best proportions to employ are—

1 lb. primrose,
12 lb. alcohol,
5 lb. water,
 $\frac{1}{2}$ lb. carbonate of soda,

heated together in a water bath.

As before stated, it fixes upon silk, and gives finer shades than eosine, more crimson, and more saturated. The silk is best dyed in water containing the soapy liquors from the silk bleaching acidified by acetic acid, raising gradually to the boil, washing, brightening with some organic acid, and drying. The dye is very fast when exposed to light, and far excels in beauty and fastness the similar colours obtained from safranine and safranum.

3. *M. Michel de Vinant on Dyeing, Printing, and Bleaching.**

Royal Blue or French Blue.—The present method of dyeing a Prussian blue upon wool was discovered in 1835 or 1836 by Messrs. Merle and Malartique, of Bordeaux. The prussiate steam blue for printing was discovered in 1838 or 1839 by M. Etienne Petit, of Rouen, who disposed of it to M. Meissonier, of Paris. M. Vinant claims for himself and M. Dajon the first application of white and orange discharge upon Prussian blue, and holds himself out as an example of an inexperienced young inventor who let the profits of his discovery enrich strangers.

For a piece of woollen cloth weighing 70 lb., take 10 lb. of yellow prussiate, which dissolve in a little water, 4 lb. salammoniac also dissolved, and $3\frac{1}{2}$ lb. of crystals of tin also in solution. In the quantity of water necessary for this weight of cloth mix 15 lb. of sulphuric acid, then add respectively the salammoniac, the tin, and the prussiate. Enter the cloth and heat up to 86° F. for the first hour, to 104° for the second hour, to 131° for the third hour, to 158° for the fourth hour, to 203° for the fifth hour, and to a gentle boil for the sixth hour; if the blue is not fully developed, 3 lb. additional of sulphuric acid may be added. Next day give it four or five ends, and wash.

For a lighter shade take, say for 72 lb. of wool, 6 lb. prussiate, $2\frac{1}{2}$ lb. salammoniac, $2\frac{1}{2}$ lb. crystals of tin, and 6 lb. of sulphuric acid; these quantities may be still further reduced for light blues. For very dark blue the following quantities and materials are given:—40 lb. of wool, 6 lb. prussiate, 6 lb. salammoniac, 6 lb. sulphuric acid, 12 lb. alum, and 6 oz. crystals of tin; the time of dyeing required is five hours.

Another dark blue is obtained by first treating the wool

* Continued from p. 27.

with stannate of soda, and then dyeing in prussiate, acid, and some tin salt. A common blue is obtained upon 40 lb. of wool with $2\frac{1}{2}$ lb. of prussiate, $2\frac{1}{2}$ lb. sulphuric acid, and 5 lb. alum, heated up for three and a half hours, and then 2 oz. of crystals of tin added, and the dyeing continued for one and a half hours longer. Several other receipts only slightly differing from these might be given, but we add only one more for light sky blue. For 50 lb. wool take 20 gallons of water, 4 lb. alum, 4 lb. cream of tartar, 1 lb. yellow prussiate, enter cold and heat gradually to boiling in two hours, then add 1 lb. sulphuric acid and 3 lb. oxymuriate.

Scarlet Dye on Wool.—This colour is either from lac or cochineal; the tin mordants are most important. The following are given by Vinant :—

Scarlet Mordant No. 1.—Three-quarter pounds common salt, 2 gallons water, dissolve and add 15 lb. nitric acid, and then gradually $1\frac{3}{4}$ lb. of granulated tin or rolled tin.

Scarlet Mordant No. 2.—Thirty pounds muriatic acid, 2 gallons warm water, 15 lb. nitric acid, 9 lb. of tin dissolved with care.

The solution of tin for preparing the lac lake for dyeing is made by dissolving $11\frac{1}{2}$ lb. tin in 71 lb. of hydrochloric acid. For 50 lb. of the lac lake in powder take 25 lb. of this tin solution and 5 gallons of warm water, and leave three or four days in contact before using. To dye 20 lb. wool scarlet with lac lake, boil three quarters of an hour with 2 lb. tartar and 2 lb. of the scarlet mordant No. 2; lift and add 1 lb. tartar, 2 lb. scarlet mordant No. 2, and $7\frac{1}{2}$ lb. of the prepared lac lake; boil one hour to one hour and a quarter; if the colour is then short of brightness some more mordant may be added, if it is deficient in depth some more of the prepared lac lake may be added. Turmeric is employed where quite fast colours are not necessary.

Cochineal Scarlet on Wool.—For 10 lb. of wool take 1 lb. tartar, $\frac{1}{4}$ lb. turmeric, $1\frac{1}{2}$ lb. of cochineal in powder, and 2 lb. of the scarlet mordant No. 2. Boil for an hour or an hour and a quarter, until the full depth of colour has been obtained.

Dark Scarlet-Pink on Wool.—Thirty pounds wool, 2 lb. white tartar, 4 lb. scarlet mordant No. 2, $2\frac{1}{3}$ lb. powdered cochineal. Boil as usual.

Light Crimson on Wool.—Thirty pounds wool, $2\frac{1}{2}$ lb. white tartar, 4 lb. scarlet mordant, 3 lb. ammoniacal cochineal, 1 lb. cochineal. Dye as usual.

Turkey Red Colour on Wool.—Sixty pounds wool, 6 lb. to 7 lb. tartar, 12 lb. scarlet mordant No. 2, 12 lb. cochineal in powder; boil for one to one and a half hours, then lift and add 10 lb. of ammoniacal cochineal, and work for another hour. Recently the ammoniacal cochineal has been replaced by magenta or fuchsine, the colour is brighter but not so fast.

A similar shade can be obtained with lac dye, brightened up with magenta to the desired shade.

Greens on wool are obtained from fustic and extract of indigo, the mordant being alum and tartar, and sometimes sulphate of alumina and tartar, for olive greens archil is added. Greens, in which the yellow part is from picric acid, are dyed with $\frac{1}{2}$ lb. picric acid, $1\frac{1}{2}$ lb. sulphate of soda, and 2 lb. sulphate of alumina for 10 lb. wool, and afterwards the necessary quantity of sulphate of indigo.

For fancy shades upon wool the three primary colours, red, yellow, and blue are mixed in the required proportions, or the wool is brought to the desired shade by superposing one colour upon another. The red part is from cochineal, the yellow from fustic, and the blue from sulphate of indigo, with sulphate of alumina and sulphate of soda as the mordanting substances, the shades obtainable are infinite.

The importance of bichromate of potash as a mordant or preparation for dyeing wool is dwelt upon. The maximum quantity to be employed is $2\frac{1}{2}$ lb. for 100 lb. of wool for dark shades and for greens, down to $\frac{3}{4}$ lb. for lighter shades of grey and drab. The author does not attempt any explanations of the remarkable power possessed by the bichromate.

Indigo Dyeing of Wool.—The method of setting and maintaining the indigo vat described by the author has been in practice some twenty-five or thirty years, and is highly recommended by him as possessing all the advantages which

could be desired on the score of the brightness and fastness of the colours produced. The vats are freshened up in the same manner from the beginning to the end, and are as good after four months' working as at the commencement; they are never run off, but every four or five months the sediment is cleared out by a sort of sack frame; three or four dyeing operations can be completed before noon, and as many afterwards without any diminution of shade or any loss of fastness in the last operation of the day.

According to Vinant it is a mistake to suppose that the best kinds of indigo are necessary to obtain the finest blues. The indigotine, or the pure colouring principle, is the same in all qualities. The difference in price of indigos being owing to the relative proportion of earthy matters and other impurities which they contain; in the indigo vat it is the indigotine alone which dissolves, all the insoluble matter precipitating to the bottom of the vat and being quite harmless in the dyeing. Attention must be paid to the temperature of the vat, a point which is usually neglected. Different dyers vary much in their practice in this respect, but it will be found that if the vat is too warm the colour will come out in the fulling.

The Indigo Vat.—If the vat be 6 feet in diameter and 7 feet deep it is filled with water warmed to 130° F., and then add $4\frac{1}{2}$ lb. of ground indigo, 34 lb. of crystals of soda (or 16 lb. of soda ash) and 67 lb. bran, the whole is carefully raked up and left at rest for twelve hours, then 2 lb. of lime, perfectly slacked, is added and well raked up, and the vat left for eighteen or twenty-four hours, the heat being kept up between 110° and 130° F.; during this time the liquor, at first blue, changes gradually to pale green and then yellow, and the scum which was white at the beginning becomes blue. The vat has a mildly acid smell which is not disagreeable. It should now be tested by dipping a sample of the stuff to be dyed in it, which should come out of a light green and become rapidly blue in the air. The indigo has been dissolved by the alkali owing to the deoxidation effected by a species of fermentation of the bran; it requires experience to know when this has been fully accomplished, and then the fermentation

must be stopped, for a continuance of it would be injurious, entering into putrefaction and leading to loss and destruction of indigo. This excess of fermentation is recognised by a disappearance of the blue froth or scum which is replaced by a colourless one, the bad smell of the liquor, absence of blue particles of indigo in the bottoms of the vat, and by testing with white cloth which acquires little or no colour by dipping. The fermentation is arrested by the addition of lime. The time chosen to add the lime is when the vat possesses the greatest dyeing power. If added before the whole of the indigo is dissolved it stops further solution of it, and the vat has a dark blue appearance from undissolved indigo. In such a case, a further addition of bran re-establishes the fermentation. The loss by permitting the fermentation to get a-head is so considerable that it is better and safer to run the risk of stopping it too soon than to wait too long, for the inconvenience in this case only amounts to the expenditure of a little more bran and waiting a longer time. It is not advisable in any case to wait until the last moment to add the lime, it can be added by portions so as to control and diminish gradually the fermentation as it reaches the desired stage, and then stop it. Generally the lime should be added in portions commencing about thirty or thirty-six hours after the bran has been added, and the vat may be seen to improve, the liquid becoming more yellow, and the scum more blue and more permanent. When all is well the vat has an agreeable aromatic odour and a taste neither acid nor alkaline, and a sample of white cloth is well dyed in it. The quantity of lime necessary is from 18 to 22 lb. The vat must be well raked up every time the lime is added and when it is heated, but the raking up must be moderate and not excessive.

When the vat is in good order, neither soft from deficiency of lime nor hard from excess of lime, the dyeing may be commenced and continued until evening when it must be refreshed by an addition of indigo to replace that which has been withdrawn by the dyeing. For each pound of indigo employed in the freshening up there must be $\frac{1}{2}$ lb. of molasses, $\frac{1}{2}$ lb.

of crystals of soda, and 3 or 4 lb. of lime added to the vat, and it should be raked up, the last raking being at nine or ten o'clock in the night. If the vat in the morning is in good condition and there is no fermentation going on, which is indicated by the clearness of the liquid and no bran floating on the top, it is not necessary to add any lime at the commencement, and dyeing may go on until noon, when the lime necessary may be added and the vat raked up; it will be ready for dyeing after dinner.

By thus freshening up every working day the vat will dye for four or five months.

When the vat is working continuously it should have an addition of $2\frac{1}{4}$ lb. each of molasses and crystals of soda every night. A vat thus properly kept up is only subject to the two defects of becoming either too hard or too soft by having too much or too little lime, the latter fault as before said is the most serious, the other can be corrected by adding more bran and waiting a few hours. A vat that has been allowed to become too soft and entered into putrefactive fermentation can be cured by addition of lime and indigo, but the portion of indigo which may have been destroyed by the said fermentation is totally lost.

The temperature of the vat must, of course, be kept up, and when re-heating, should be raised to a temperature of 120° or 130° F. The proper temperature for regular working is from 110° to 118° F. If worked hotter the blue will be darker and more purple, but it will not be so fast to soap.

At the end of four or five months the bottoms must be removed, but the clear liquor is still good, and may be used for setting a new vat, which then requires only half the quantity of materials indicated at the commencement.

This vat has entirely supplanted the older vat, in which madder and pastel or woad were used. Madder was only useful from the fermentescible matters in it. The colouring matter was no use, but molasses are much preferable as being cheaper, and not filling up the vat.

Molasses and lime alone dissolve indigo perfectly and completely, but the addition of carbonate of soda is useful; for

however well the wool has been bleached, it retains always some greasy matters, which are acted upon by the soda, partly caustified by the lime, and which favours the entrance of the indigo, giving fuller and faster colours.

In treating of the dyeing and printing of delaines or goods containing both cotton and wool, we were perplexed at finding several times the prescription of passing the goods at first in stannate of soda, and then washing off without any acid. The ordinary stannate of soda used in England would give little or no tin to the cloth by such a treatment; but we find at page 219 a receipt for the preparation of the so-called stannate of soda, which, the author says, is, without contradiction, the best that can be employed for preparing or mordanting goods for either printing or dyeing. It is composed of 7 lb. of oxy-muriate of tin mixed with 3 gallons of caustic soda at 30° Tw. for one part, and 11 lb. of oxalic acid dissolved in 1 gallon of water for the other, the two solutions being mixed together and reduced by water to the proper strength, which is $1\frac{1}{2}^{\circ}$ B. for mordanting loose, and 6° for preparing by padding without pressure. The padded goods are simply left twelve hours cool and then washed off. We do not give any of the great mass of receipts for dyeing these goods, not observing any particular novelty in them, and because they are not accompanied by any explanatory text. We may, however, observe that sulphate of alumina (patent alum) is much used, that salt being readily obtained on the Continent quite free from iron, and, moreover, that sulphate of soda is nearly always employed in conjunction with the sulphate of alumina.

Yarn Dyeing.—A mordant to be used for dyeing in some of the aniline colours consists of 100 lb. of sulphate of alumina, dissolved in 12 or 13 gallons of water by boiling, avoiding copper vessels. Then 12 lb. of sulphite of soda are thrown in at once, and well stirred up with a wooden stirrer, and the whole boiled for at least two hours. The liquor is then filtered, and is very concentrated. It should be reduced to about 12° Tw. for steeping the yarns, which remain in the fluid five hours, and then washed and immediately dyed. The use of sulphite of soda seems unusual and not very rational. The

author, however, praises it as being superior to sumac, stannates, acetate of alumina, oleine soap, tin solutions, oil mordants, and other substances in use for preparing cotton for anilines.

Black for Bobbin Cotton.—Ten pounds of the cotton, first boiled for six hours in water alone to clean it, then dipped seven times in a bath containing 2 lb. of logwood extract and 12 oz. of dark catechu heated to about 160° F.; leave in the liquor covered up all night. Then, without washing, enter into a solution just warmed of 3 oz. of sulphate of iron and 3 oz. of sulphate of copper; lift, leave in a vessel for half-an-hour, and pass in a warm solution containing 3 oz. of bichromate of potash; leave to drain for an hour, and wash well. Pass again in the original logwood and catechu, to which some fustic extract may be added; leave two hours, and without washing pass in cold chrome, and wash; soften by emulsion of oil and soda, or in soap and water.

Another Black on Yarn.—For 20 lb. of cotton, give seven turns in sumac liquor at 104° F., the sumac being at the rate of 8 lb. per 100 lb. of cotton; lift, air, and wring. Give nine ends in a clear solution of calcined copperas, dissolved at the rate of 3 lb. for 100 lb. of cotton. Lift, wash well, and dye in logwood, taking 40 or 45 lb. per 100 lb. of cotton. Lift, leave for one hour, wash and soften as above.

Aniline Black upon Yarn.—This process requires great care in the working, or the colour will be uneven. By proper attention, a very fine black can be obtained. However, I may confess that, say once in ten times, I got only a bad result. The cotton being well scoured, take for each pound one-fifth of sulphate of copper dissolved in water slightly acidulated with hydrochloric acid. Give seven ends and wring well. Pass for five ends in a solution of hydrosulphate of soda at $\frac{1}{2}$ lb. per gallon heated to 120° F.; wash well. Dye cold in sufficient water containing 3 oz. of chlorate of potash, 3 oz. of salammoniac, $\frac{1}{2}$ lb. of muriate of aniline. Pass the cotton rapidly seven ends, wring well, and beat. Hang up very evenly in a room heated to about 77° F. for forty-eight hours, and afterwards increase the heat to 86° F. Pass in either

bichromate or in weak soda, and wash very well. If the black, after drying, is reddish, it may be improved by treatment with very weak chloride of lime solution.

4. *Upon the Artificial Colouring Matters of MM. Croissant and Bretonnière.*

THESE colouring matters form the subject of an English patent dating 24th April, 1873, upon which the £50 stamp duty necessary to keep the patent valid was paid in due course some months ago. The announcement that colouring matters possessing great stability and powers of resistance to the action of light, air, and detergents, could be produced from such a material as sawdust by the action of inexpensive agents like sulphur and soda was naturally received with considerable interest by all interested in textile colouring. When it became known from the specimens exhibited that the colours yielded did not present any novelty in shade, that they belonged to what may be called the catechu class of colours—browns, drabs, and greys—and that they did not possess brightness or brilliancy, they almost immediately fell into neglect, and but little has been heard of them for some time past. A recent report by M. R. Glanzmann* shews that attempts are still being made to apply these colours, and it is thought useful to draw up an abstract of what has been published concerning them.

A lengthy paper upon this subject was read to the Industrial Society of Mulhouse by one of the patentees on the 30th December, 1873.† The first idea of the experimenters was to try and obtain some new modifications of well known colours, and they commenced upon the solid extracts of logwood, peachwood, quercitron bark, and catechu, and considering that all these substances contained varieties of tannin, and that gallic acid was really a product of tannin, they had the

* Bulletin de la Soc. Ind. de Rouen, iv., p. 61.

† Bulletin of the Society, xlv., p. 465.

idea of treating the extracts as gallic acid is treated when it is desired to transform it into metagallic acid, that is by simple exposure to heat and air at about 500° F. At this temperature oxygen was absorbed, carbonic acid evolved, and they obtained from logwood extract amongst others a bulky, spongy, black mass, very light, totally insoluble in water, but easily soluble in alkalis, and possessing generally the properties of metagallic acid.

In further experiments caustic soda was added to the extracts and the mixture heated, the alkali facilitated the action in a remarkable manner and the same product was more easily obtained, and was used for dyeing cotton and linen yarn in the year 1868. The experimenters then operated upon other organic matters such as starch, farina, bran, sawdust, &c., in the same way, *i.e.*, with addition of caustic soda, but no colouring matters were obtained.

They then thought of adding some agent to the soda which would be capable of removing hydrogen from the organic substances, and having tried iodine, bromine, and sulphur, fixed upon the latter as most proper for their purpose and at length succeeded in producing a series of bodies which they call *organic sulphurets*.

There is scarcely an organic substance which, under the influence of soda, sulphur, and heat, does not yield a matter which can be used in dyeing; amongst the materials acted upon were sawdust from common woods, humus from decayed oakwood, horn, feathers, refuse of wool and silk, sugar, glucose, starch, gluten, flour-starch, lichens and mosses, cotton waste, tannin, gallic acid, gelatine, milk, lactarine, animal excrements, urea, soot, the organic acids, aloes, gum dragon, gum lac, gum arabic, tragacanth, dextrine, glycerine, and others.

In some cases it was found that the sulphur entered directly into combination with the organic substance without displacing any of its elements, the temperature employed not much exceeding 212° F.; aloes is an example.

In the great majority of cases the sulphur combines with the hydrogen of the organic substance, sulphuretted hydrogen

is evolved, and the place of the hydrogen is taken by sulphur, the temperature required may be 480° F. to 580° F., or even higher; sawdust is an example.

As a general rule the more the operation is pushed by heat and the greater the proportion of sulphur employed the darker are the products obtained, and M. Chevreul reports upon the dyed and printed colours that those yielded by the more extreme processes are the fastest when exposed to light and air.

The products are very hygrometric, and must be preserved from free contact with the air, for they become speedily injured by absorption of water and oxygen. The same thing takes place if they are dissolved in water, and kept for a length of time. It is observed that freshly-prepared solutions of these dye stuffs shew a strong affinity of the colouring matter for fibre, upon which it fixes without the assistance of a mordant, and so complete is this affinity, that by prolonged contact with fibre the solution becomes nearly colourless; but after a while this affinity diminishes, and old solutions made, say four or five months, do not dye at all, the colouring matter being precipitated. To obtain the best results from these colours, they should, therefore, be freshly dissolved in soft water; hard water precipitates the colouring matter.

The method of dyeing consists of working the cotton for half-an-hour in warm liquor containing a sufficient amount of the colouring matter, wringing out, and working hot for half-an-hour in solution of bichromate of potash, washing, and lastly boiling in solution of carbonate of soda.

The colouring matter obtained by acting upon the humus of decayed wood of old oak trees has an extraordinary affinity for cotton fibre, dyeing the darkest shades at one operation, and giving the fastest colours. The specimen of yarn dyed with this substance (inserted in the text, p. 474) shews a colour much resembling a medium manganese brown. It is dull, and without depth. Bran gives a colour which dyes a dark catechu brown, which, by boiling with carbonate of soda, acquires a greyer tint; but neither of the shades, as illustrated by dyed yarn, can be said to be good.

The chief material, however, is sawdust, preference being given to that from woods containing the least amount of resinous matters, as the oak, beech, cherry, and chestnut. The sawdust must be dried and finely sieved. After treatment with soda and sulphur, it yields a soluble product of a dark brown colour, without odour, and which dyes fibre of a dark greenish grey. After chroming, it is not changed by boiling carbonate of soda, and is fast to air and light, to acids, alkalies, and soap.

Sawdust which has been degged with urine, and kept several months, yields a greenish-black material, having a great affinity for fibre, which it dyes of a grey more or less deep, which, when chromed, has a catechu grey colour. It is changed by boiling in carbonate of soda, retaining its intensity, but acquiring a purplish hue. It is noticed that if the primary material contains nitrogen—for example, bran, flour, &c.—the shades dyed are always more or less modified by the boiling carbonate of soda.

The product obtained from sawdust and an alkaline sulphuret heated to a high temperature is very soluble in water, has a most remarkable tinctorial power, and gives shades of great fastness, even when light and delicate.

There are two samples of dyed yarn to illustrate the colours, one dark and the other light. The dark may be characterized as a brownish black, or a very dark chocolate. The colour is not bright or agreeable. The light shade is nearly the colour of unbleached linen yarn, tolerably bright and pleasant. Aloes give a purplish grey, which, from the sample given, cannot be said to be a very desirable shade.

Tartrate of soda gives very surprising results. Itself quite colourless, it acquires by the action of sulphur remarkable dyeing powers, and is capable of yielding different colours. The product is very soluble in water, in which it dissolves with a fine emerald-green colour. Cotton dyed in it acquires a tobacco-brown shade, which, by the action of boiling carbonate of soda, changes into a good bluish-grey, while the soda solution becomes coloured green.

Logwood extract treated by the process gives a colouring

matter of great power, the solution of which may be kept a long time without being injured. The greys and blacks which may be obtained from it are very fast, and are comparable to those obtained from aniline. At the conclusion of this paper, of which we have given a condensed abstract, the patentees say—"The majority of the colours which we have obtained have certainly neither the purity nor the brilliancy of the aniline colours. They are generally compound shades, which, however, are suitable for a great number of purposes. They may be advantageously combined with other colours to darken them, and to give them what is known as a 'fast bottom.' Amongst them are a certain number of remarkable fastness which may be profitably employed in the colouring of goods which are required to resist the action of alkalies and frequent washings. The manufacture of these products is uncommonly simple, requiring no costly materials, nor special apparatus, and it may be hoped that they are worthy of attention of both practical and scientific men."

The chemical section of the Industrial Society of Mulhouse appointed Messrs. Schaeffer, Brandt, Scheurer-Rott, Witz, and Rosenstiehl to study and report upon this invention. They made their report to the meeting on the 25th March, 1874, and the salient points of it are as follows:—The reporters were interested in the examination of colours practically used for dyeing drills or ticking, and which was so resistant as to permit an ink stain to be removed from the dyed goods by means of oxalic acid without injuring the colour itself. There are very few colours which are not, in part at least, removed by the action of acids. They found cotton took the dyes very readily and very evenly, and that defects in bleaching which would cause many self-colours to be cloudy or uneven, had no injurious action here. After trying many of the preparations and various methods of fixing, they found all the shades were dull, and not differing much from one another. None of them were as bright as catechu colour, the nearest to catechu being that made from Cuba wood, and prepared by the reporters themselves. All the colours, when fixed by chroming, possessed a degree of stability rarely found with vegetable colour-

ing matters. Light does not act sensibly upon them for a long time. Boiling soap does not produce any noticeable change. Boiling alkaline solutions alter the shades to greys of a greater or less degree of purity, seeming to remove a small quantity of a brown colouring matter.

Oxalic acid dissolved in four times its weight of water has no action upon the colours, which renders it possible to remove an ink stain from a dyed colour without leaving any trace of its action. Chlorine and hypochlorites destroy the colours rapidly.

The products of Messrs. Croissant and Bretonnière did not give to the reporters any shades of colour which could not be obtained by well-known methods long in use, but they have an advantage in facility of application, remarkable fastness of colour, and moderation in price.

Applied by roller, thickened with dextrine or tragacanth, and prepared in various ways, it was found that the colouring matter fixed rapidly even during the printing; by steaming a more perfect fixation was obtained, but chroming was not found necessary; preparation of the cloth with mordants was no advantage, not changing the result. In no case could dark colours be obtained. If as much as 15 per cent. of the solid colouring matter was employed in the colour used, there was no increase in the fixation of colour, the excess washing off.

If the colouring matters were subjected to a sort of purification by precipitating with acid, washing, and dissolving in alkali, they gave greys of a slightly yellowish tinge, resembling carbon greys, this difference in tint apparently being due to the removal of brown matters in the raw product. The reporters did not know whether this treatment was advisable or not. It yielded more uniform shades, and the colour did not act so much upon the roller; but, on the other hand, there was a want of variety in the shades produced from the various preparations.

It is concluded that these colouring matters have an undeniable interest from their stability and easiness of application in dyeing, and would probably find an immediate

employment in simple goods which required great fastness of colour. For printing purposes their utility is doubtful; the shades have not sufficient variety to permit of an extended application. If it had been possible to obtain a black from these colours no doubt it would have been very valuable, judging from the properties possessed by the other colours. It would have been faster than a logwood black, and not have gone green by acids like aniline black.

There are four specimens of prints attached to the report, shewing the colours made by employing 6 per cent. of the dry products of wood, flour, logwood extract, and humus of old oak in the thickening matter. They are drabs of different intensity, but with little or nothing to recommend them except their fastness.

Such was the extent of our knowledge upon these colouring matters up to October, 1874. We have now something additional from the paper of M. Glanzmann, which was read before the Industrial Society of Rouen, 4th February, 1876. He was induced to repeat and continue the researches upon these matters on account of the appearance in trade of a new substance called "laval catechu," issuing from a well-known manufacturing house (Poirrier). This substance was in large broken masses, resembling partially carbonized wood, very porous, of a black-blue colour, and emitting an odour of sulphuretted hydrogen. It was contained in tin boxes and was found very hygroscopic, dissolved easily in water, which when warmed took up one-fourth of its weight; beyond that quantity it mixed rather than dissolved in water. The solution was very alkaline, precipitated by all acids, which in excess caused an evolution of sulphuretted hydrogen; concentrated mineral acids separated sulphur from the solution, which by heat melted and swam on the surface. The precipitated matter is always of a dark brown colour, and is with difficulty redissolved by alkalies. Most of the metallic salts and acid salts also precipitated the colouring matter either black or dark brown, mixed with the metallic sulphuret and oxide carried down by the alkali.

The experiments in printing this colour were not particu-

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larly successful, but brought out some new facts, which, however, do not seem capable of receiving an extended application. The experiments were in four series.

In the first a colour thickened with starch and containing 4 oz. of the organic sulphuret per gallon was printed. It gave a dull grey.

The colouring matter fixes perfectly without assistance of mordant, simple contact with the fibre is sufficient to dye it. Steaming helps the fixation, for samples steamed were found to lose much less colour in washing out the thickening.

Chroming, either hot or cold, in bichromate at 1 lb. salt to 20 gallons of water after steaming accomplishes the complete fixing of the colour, so much so that colour thus fixed appears as dark as after the printing. The goods may also be washed off in weak mineral acids, without changing the colour; alkaline baths also can be used without any injury taking place to the whites. The grey colour resulting resists in a perfect manner the action of light, mineral acids, and soap. Bleaching powder solution has more action, a sample sent through the chloring machine with chloride of lime at about 1° Tw. lost at least 20 per cent. of colour and became yellower. Upon stronger colours less action takes place.

The second series of trials were made with a view of determining the best thickening, and to ascertain the effect of preparing the cloth with mordants.

Three different thickenings were employed—white starch, gum substitute, and tragacanth jelly. Colours containing 1 per cent. of the colouring matter were printed upon unprepared calico, upon calico prepared with acetate of alumina from precipitated alumina at 12° Tw., and upon calico prepared with weak tannic acid.

The thickenings with starch and tragacanth gave the best results. The colour thickened with gum substitute does not fix, all disappearing in the washing; this is owing to the acidity of the thickening which ought to be alkalized before adding the colouring matter.

The preparation of the cloth had not the least influence upon the shades produced. Steaming and chroming have a decided

influence in fixing the colour, but in weak shades give a strongly yellow tone to the colours.

None of the results obtained by printing are worth anything. The shades have an unpleasant yellow aspect, to correct which it is necessary to wash off in weak acid or in sulphate of copper as will be shewn further on.

The third series was upon mixtures of the new colouring matter with some other colouring matters soluble in alkalies. Catechu and annatto give some good shades; annatto appears to resist light much better in this combination, since a sample did not lose much colour by eight days' exposure to the sun. The mixed colours must be steamed, and the catechu colours chromed; the annatto mixture may be passed in weak acid after steaming.

The remaining trials were an endeavour to combine this colour with dip-blue styles, but the results were not satisfactory. Printed as a crossover it darkens the indigo where it falls, but the yellow shade of the colour gives a greenish hue to it. By using a stronger blue, steaming, and passing in sulphate of copper, somewhat better results were obtained. The grey partially resists the discharge of oxalic acid and bichromate upon indigo, and some interesting effects can be obtained, but, on the whole, there seems little hope of being able to make any profitable use of this colour in printing.

In dyeing, the prospects are much better, for M. Glanzmann says there is no colouring matter known so fast and so easy to apply, and which can give so many different shades. These properties, combined with its low price, make it deserving of attention.

For dyeing, yarn, nothing more is required than to dip the cotton a few minutes in a solution of the colouring matter. Wash, and pass in the fixing agent so as to obtain the shade desired. The depth of colour obtained is exactly in ratio with the degree of concentration of the colouring matter, and independent of the volume of the solution or the total quantity of colouring matter present; and in this respect it differs from nearly all other dyestuffs.

It is possible to vary the shades by varying the fixing agent,

which may be bichromate of potash, carbonate of soda, metallic salts, or weak mineral acids. It is observed that nitrates and nitric acid give a yellow tone to the colours, while sulphuric acid and the sulphates, especially sulphate of copper, yield bluer tints.

The cotton has always a soft agreeable feel when finished in any of these solutions.

The colour obtained by dyeing at about 170° F. in a solution containing 5 per cent. of the colouring matter, and fixed in bichromate solution at 1 of salt to 200 of water, is a good dark shade. The colouring matter at 3 per 1,000 gives, in the same way, a good light grey of remarkable solidity.

The best shade of grey is produced when the dyeing is finished in sulphate of copper solution containing 1 per cent. of salt.

By combining catechu in alkaline solution with the colouring matter, and also annatto, some compound shades possessing desirable qualities may be obtained.

The bluish grey obtained by finishing in sulphate of copper may be advantageously used as a basis for dyeing in indigo blue to obtain darker shades with economy. It is not less stable than indigo itself, which is one of its recommendations for this purpose.

These colouring matters appear to have been already extensively used for dyeing in Germany, a manufactory at Goettingue producing them on a large scale, and supplying eighteen different colouring matters obtained from various matters by the sulphuret of soda process.

5. *Schützenberger and Lalande's Indigo Blue Process.*

THE practitioners of every art and the adepts in every science, from medicine to mathematics, have to acknowledge something incomplete in their methods or their proofs—something

which seems easy or evident, but which persistently eludes satisfactory performance or rigorous demonstration. The art or the science of calico printing has also its unfilled gaps, or, as it is said, its reproaches, and one of the chief concerns the topical or direct application of indigo blue in printing. This is one of the most ancient colouring matters, and one of the most valued. As applied to dyeing, it is also one of the most manageable and most satisfactory ; but when the printer tries to bend it to his purposes he finds it, if not quite unyielding, at least so stubborn, so difficult, and so uncertain, that, notwithstanding all the brilliant honours and rewards that are promised to success, he finds himself baffled, and, so far as he has gone, it may be said, either quite defeated or retiring from the effort with such glory as may be claimed from a costly and barren victory.

We do not propose to give a history of the various ingenious and strenuous attempts which have been made within this generation to accomplish the printing of indigo, either alone or in combination with other colours, but merely refer to the separate processes of Woodcroft, Philippi, Ward, and Lightfoot, each of which was put into practice, and each of which, after severe struggling, has been obliged to retire in the face of unconquered difficulties, not without something to show for honour, but, it is feared, nothing to show for profit. We do not say that this is to be the fate of the process mentioned at the head of this article. We have looked on with interest at what has been done by it, but we must confess with very little hope ; and though it, and perhaps some of the other processes mentioned are still in use here and there, we have no proofs that it has met with a genuine practical success.

The best account of Schützenberger and Lalande's process is that given by M. Ch. Gros-Renaud in the Bulletin of the Industrial Society of Rouen, vol. ii., p. 17. The writer speaks from a practical knowledge of the subject, and we think it desirable to give the paper nearly in full. As soon as the process was made known, the editor, following the instructions given by the inventors, prepared some of the colour, and had it printed, but having experience of the old gas blue process

of Woodcroft, and practical knowledge of Lightfoot's method on the large scale, he felt quite satisfied with the first trial of the hydrosulphite blue that it was not any substantial improvement upon the old orpiment blue; that it would have nearly all its weaknesses without some of its strong points; and though quite different in its principle of application to Lightfoot's process, it would present equal, if not greater, difficulties when applied along with mordants.

But we will let M. Gros-Renaud speak:—The principle upon which the process rests is founded, like all the methods of obtaining a fast blue, upon the property of indigo being changed by reducing agents to the state of white indigo, soluble in alkalies and alkaline earths. The white indigo being obtained, is then mixed with the solvent and a sufficient quantity of the reducing matter to prevent oxidation during the handling and printing of the colour.

It is true that the great affinity of white indigo for the oxygen of the air in this process, as in all similar ones, causes considerable difficulties in practice; but these need not be exaggerated, nor should failure at the commencement bring condemnation upon the methods. As an example of difficulties surmounted, among many others, may be cited aniline black, or artificial alizarine, and it is not wise that the first difficulties or a few bad pieces should cause us to renounce a process offering incontestible advantages with reference to manipulation and promptness.

The subject is treated under several heads as follows:—

Preparation of the Acid Hydrosulphite of Soda.—The so-called hydrosulphurous acid was discovered by M. Schützenberger. It has a great affinity for oxygen, and is consequently very unstable. To prepare the acid salt of soda, vessels like carboys or bottles, which can be closed securely, are filled up with zinc, granulated or in turnings, and then the interstices filled by pouring in bisulphite of soda, smelling strongly of sulphurous acid, at 54° Tw., observing that the vessels are full to the neck. These two bodies are left to react upon one another for an hour, and, if possible, the vessels are turned over two or three times during the operation, so as to mix up

the contents. The bisulphite in this manner yields the maximum amount of hydrosulphite, which marks about 60° Tw. This operation must be made when required, that is, when all is prepared for employing at once the acid hydrosulphite thus obtained. It cannot be kept, and therefore cannot be prepared in advance.

The zinc is best in the state of cuttings from sheets. Zinc powder is very irregular in its composition, and acts too rapidly, heating the mass considerably. Granulated zinc is inconvenient on account of the difficulty in cleaning it for a continuance of the operation. To prepare for a second operation on bisulphite, the liquid is poured off the zinc unacted upon, and the zinc washed first with water, and then with hydrochloric acid, to remove an incrusting matter formed by the action of the bisulphite. The zinc dissolved is equal to 3 per cent. of the weight of bisulphite operated upon, and this loss must be made up by fresh zinc. It is repeated that to get regular results the hydrosulphite must be used freshly prepared.

Preparation of Neutral Hydrosulphite of Soda.—For each 10 lb. weight of acid hydrosulphite of the previous operation take $3\frac{1}{2}$ lb. of milk of lime, which contains 2 lb. of quick lime per gallon, and having placed it in a bottle or cask, add the acid hydrosulphite, and arrange the proportions so that the bottle or cask shall be quite full. Secure the opening, and agitate well to mix the lime and liquid. If the mixture becomes much heated, it may be advisable to cool the vessel in water.

The neutralized hydrosulphite keeps better than the acid, and may be prepared the day before being required. It has been found good even at two days' age. It must be alkaline in order to keep. When it is required to use the neutral hydrosulphite, the mass resulting from the mixture of lime and acid hydrosulphite is taken, and the clear liquor pressed out of it by means of strong pressure either in straining cloth or in sacks. It should stand about 32° Tw.

The substitution of soda for lime in this process is not advantageous, and the precipitate is more bulky than with lime.

Reduction of the Indigo.—Two pounds of good Bengal indigo

(or any other quantity) are ground as usual in the indigo mill with so much water that there shall be 1 lb. of dry indigo in 1 gallon of the liquid. Take 2 gallons of this ground indigo in a 6 or 8 gallon pan, and add 5 to $5\frac{1}{4}$ lb. of caustic soda at 63° Tw., and 14 lb. of the hydrosulphite. Heat the whole up to about 165° or 170° , and keep at that temperature for fifteen or twenty minutes.

Now procure a funnel with a neck long enough to touch the bottom of the pan, and pour down it $3\frac{1}{2}$ lb. to $3\frac{3}{4}$ lb. measure of hydrochloric acid, stirring all the time.

During the addition of the acid a large quantity of sulphurous acid is evolved which may prove inconvenient to the operator, unless it be done in the open air, or under a chimney with a good draught. When the decomposition is completed, which is shewn by the liquor being acid, the whole contents of the boiler are transferred to a tub holding 15 or 16 gallons, which is filled up with common water. The next morning the clear water is drawn off as closely as possible to the precipitate, and the tub is filled up afresh with water, to which about $\frac{1}{4}$ per cent. (1 quart per hundred gallons) of hydrosulphite had been previously added. This addition is not, however, indispensable.

The following day the precipitate is collected on a filter and washed. When well drained, the precipitate should weigh 7 lb. from 2 lb. of indigo, and is called the dense precipitate. Formerly other strengths were used, but they have all been discarded for this one, which suffices for all the requirements of fast blue.

Making of the Colour.—The importance of employing a good quality of indigo is known to all those acquainted with those colours, but a neglect of this point was the cause why a very important English house completely failed in the application of the process we are treating of. The nature of the precipitate has also a great influence upon the results. The numerous experiments we made upon the best kind of precipitate led us to the one indicated above. It is the least subject to oxidation in the air, and is the most easy to manage. Moreover, this paste does not require pressing, which is a very

inconvenient operation ; for at the strength of 2 lb. of indigo in 7 lb. of precipitate it is concentrated enough for the darkest colours.

The precipitate is best preserved from oxidation by mixing it with gum water, 2 gallons of gum water to 7 lb. of precipitate forming the standard afterwards referred to. Senegal gum water appears to be the only suitable thickening agent.

Direct Colours.—These are made without precipitation in the following manner :—Place in a boiler $3\frac{3}{4}$ lb. of the ground indigo pulp containing at the rate of 2 lb. of dry blue indigo in $1\frac{1}{2}$ gallons of pulp. Heat, and add 3 lb. of gum in powder. When dissolved, add 5 lb. of neutral hydrosulphite and $\frac{1}{2}$ lb. of milk of lime (containing 2 lb. of dry lime per gallon). Heat to 160° F. for twenty minutes, and then cool down to 95° or 100° F., and add $1\frac{1}{2}$ lb. of neutral hydrosulphite and $\frac{1}{2}$ lb. of milk of lime—the whole making 14 lb. of colour.

The following are receipts for colours made from the precipitated indigo:—

Thick Colour at $6\frac{1}{2}$ oz. Indigo per gallon.

- 2 gallons of the standard previous.
- 6 lb. acid hydrosulphite.
- $3\frac{1}{2}$ lb. milk of lime (2 lb. dry lime per gallon.)
- $5\frac{1}{2}$ lb. neutral hydrosulphite.
- 2 lb. gum water.

Gives 36 lb., or about $3\frac{1}{2}$ gallons colour, which should be gently warmed.

Fine Colour at $6\frac{1}{2}$ oz. Indigo per gallon.

- 2 gallons of the standard.
- $10\frac{3}{4}$ lb. of the neutral hydrosulphite.
- $1\frac{3}{4}$ lb. of the milk of lime above.
- 2 lb. gum water.

Gives about the same amount of colour as above ; should be warmed to about 90° F.

Fine Colour at 5 oz. Indigo per gallon.

- 1 gallon of the standard.
- 6 lb. gum water.
- 7 lb. neutral hydrosulphite.
- 1 lb. of the milk of lime above.

Fine Colour at 2½ oz. Indigo per gallon.

- 4½ lb. of the standard.
- 8 lb. neutral hydrosulphite.
- 6 lb. water or gum water.
- 6½ oz. caustic soda, at 64° Tw.

The caustic soda to be as pure as possible; the colour warmed up as above.

Dextrine Colour at 2½ oz. Indigo per gallon.

- 1 lb. of the precipitate not mixed with gum water.
- 14 lb. to 15 lb. of light dextrine gum water.
- 5½ lb. neutral hydrosulphite.
- 6½ oz. caustic soda, at 64° Tw., or same quantity of milk of lime.

In all the colours the milk of lime may be replaced, if it is thought any advantage, by the same weight of caustic soda at 64° Tw., but the caustic should be of very good quality, and made either from crystals or the best soda ash.

In all the colours it is indispensable to have a great excess of the hydrosulphite present, for it must not be forgotten that in the working a considerable portion of the hydrosulphite becomes oxidized, and converted into sulphite. To counter-balance the oxidizing action of the air, and to keep the indigo reduced, the best quantity of the neutral hydrosulphite to use is 3½ lb. per gallon of the dark colour, at 6½ oz. indigo per gallon; if it were not for this difficulty 2½ lb. would be quite sufficient.

It must also be observed that in the colour in question a certain quantity of lime is absorbed or disappears, for it is found that 33 grammes of the milk of lime are capable of dissolving the precipitate representing 40 grammes of indigo, but this quantity must be nearly doubled to get regular and practical results. This observation found in practice is in contradiction to the experiments on the small scale made at the commencement, for it is known that the neutral indigotate of lime is more soluble than the basic indigotate, and with 33 grammes the neutral salt is formed, while 53 grammes gives the bibasic salt; this fact requires elucidation.

Beyond a strength of 4 lb. indigo blue per 10 gallons of

colour it is useless to go ; 5 lb. to 10 gallons does not give a proportionable result, but probably it may be useful to print such a colour in fine patterns, when the darkest obtainable shade is required.

The colours can easily be reduced ; the author has frequently printed colours reduced more than one half from the strength. The pale blues are very reliable, for the simple reason that one is not confined to such narrow limits in the quantity of hydrosulphite which may be added, and an excess is always advantageous.

In whatever manner prepared, the colours must be worked warm in order to produce good results. It is proved beyond doubt that the warmed colours are not acted upon by the air. The best temperature for working is between 86° and 95° F. It is useless to go higher than 95° , and it is unsafe to work the colour below a temperature of 86° . This point is of great importance, for by attention to it we have been able to print eight to ten pieces without having to empty the box.

Treatment of the Printed Pieces.—A good colour does not develop itself very quickly after printing. I have observed that the best results have been obtained when the greenish tint has remained until the following day. The fine or thin colours give better results than the others, because they do not froth so much ; and it is found preferable to work without furnisher in the colour box. In winter the rollers should be warm before commencing to work.

The printed goods may be hung up until the next day, or at once passed in a very weak chrome liquor, in either case suspended in running water for half an hour, then washed and soaped for thirty or forty minutes at 120° to 140° F. If the white requires it the goods may be chlored without injury.

If the hydrosulphite blue is associated with other colours in special styles, the goods are submitted to the regular operations required by the associated colours without any special attention to the blue, for it is found that passing in soda, carbonate of soda, sulphuric acid, chrome warm and cold, or chrome and lime, silicate of soda, or other dung substitutes, or dung, have no perceptible action upon the blue.

The blue colour has been blamed for its great liability to change; it is true that it is very liable to extremely rapid changes, either by exposure to air or by careless manipulation. However, it may be stated that a portion of colour prepared in France was sent to England, where it was worked with good results. Another portion of 12 kilos. was despatched to America in a perfectly closed glass vessel; it was not tried for two months after its arrival, when it gave excellent results. The author states that he has frequently found colours which had been worked, in fair condition three or four days afterwards.

With regard to the most serious complaint against the colour, that when a single piece has been printed a change takes place in the shade, and that two pieces cannot be printed of equal shade from a box of colour, the author states that it is not well founded, and shewed to the Society samples from the first and tenth pieces printed at one time without emptying the box, and which presented very trifling differences in shade; and he maintains that it is possible, by attention and experience, to overcome the difficulties which appear at first. One thing he mentions as important, and that is, to keep the colour at the same level in the box while working, and pretty high, which prevents frothing in a great measure. If the frothing becomes too bad to go on, the colour must be taken out of the box, and the indigo recovered from it by subsequent treatment.

Several illustrations of the colour alone and combined with aniline black, garancine chocolate, madder red, chrome orange, and, as a cover over, a three-colour garancine pattern with resist red, black, and chocolate, are shewn—all very good for the style.

The author had not been able to combine the blue with steam colours, for during the steaming a portion of the indigo was destroyed by some obscure action not yet known.

Trial of the Bisulphite and Caustic Soda.—The results obtained from various samples are very different, according to the purity of the materials supplied. To avoid irregularity from these materials, the following rapid and practical process is proposed for testing these products:—In a flask with a narrow

neck, which can be hermetically closed, 20 grammes of indigo in fine powder are placed, or an equivalent quantity of indigo pulp; then 200 grammes of warm water added, and 100 grammes of caustic soda at 64° Tw. The whole being well mixed, the flask is put on the scale of a balance, and then 100 grammes of acid of hydrosulphite made from the bisulphite under examination is added. If the reduction takes place in a few minutes, and as quickly as in a comparative trial made from a bisulphite of known goodness, it may be concluded that the sample under examination is suitable.

This trial serves two purposes—1, to determine the richness of the soda, and, 2, that of the bisulphite of soda; for the less strong the soda, the more it will require for the bisulphite; and reciprocally the less concentrated the bisulphite, the more it will require to reduce the indigo. M. Schützenberger proposes a standard solution of copper and ammonia as a more exact method of analyzing the hydrosulphite. It is made from 600 grammes of hot water, 100 grammes of sulphate of copper, and 300 grammes of strong ammonia. Permanganate of potash can also be employed.

Recovery of Indigo from Colours.—One of the advantages of the hydrosulphite blue is that the indigo can be readily recovered from spoiled colours. The author had recovered 17 kilos. from the commencement of the process. The method is as follows:—In a pan or boiler of a capacity of 40 gallons put 8 or 10 gallons of the spoiled colour, adding about 26 gallons of water. Boil, and add a mixture of 10 lb. of sulphuric acid and 2 gallons of water. Continue to boil for about an hour, or until the effervescence and evolution of sulphurous acid has ceased. The liquor is then put into a large vat full of water. The deposited indigo is washed by decantation until it is neutral. It is then collected on a filter, and may be employed over again.

The cost of the hydrosulphite blue is estimated as much less than that of the blue made by oxide of tin. The experiments at Scheurer's shewed an advantage of 60 per cent. in favour of this process.

6. COLLECTED RECEIPTS.

INDIGO COLOURS AND VATS.

No. 146.—China Blue.

The standard is 4 lb. indigo ground in 1 gallon water and 2 quarts of muriate of iron at 80° Tw. The colour, 1 measure of the standard to 3 measures of gum water. This is of English or Scotch origin, and from an anonymous printed collection of receipts published in Philadelphia.

No. 147.—China Blue (Bleu Fayence).

10 gallons hot water—50 lb. green copperas—25 lb. acetate of lead; dissolve and let settle; thicken the clear with gum Senegal very thick. Indigo, 1 lb., ground up well, with 3 quarts of the acetate of iron above— $\frac{1}{2}$ lb. crystals of tin—1 gallon of the thickened acetate of iron.

Process of fixing—(1) lime—(2) copperas liquor, at 6 lb. per 10 gallons—(3) strong lime vat—(4) copperas liquor, at 11 lb. per 10 gallons—(5) caustic soda or potash 14° Tw.—(6) sulphuric acid, at 4° or 5° Tw. From a French manuscript.

No. 148.—China Blue.

1 lb. indigo, best quality—1 lb. sulphate of iron (green copperas)—1 quart water. Grind well together, and add 4 lb. iron liquor at 14° Tw.— $\frac{1}{2}$ pint water; heat gently up to 140°, and thicken with gum.

Process of fixing.—There are four vats. (1) lime—(2) sulphate of iron at 10° Tw.—(3) caustic potash or soda—(4) sulphuric acid at 4° Tw. Three dips alternately in the first and second vats of 15 minutes each; thirty minutes in No. 3 vat; and fifteen minutes in No. 4. From a French manuscript.

No. 149.—Dark China Blue.

12 lbs. indigo—2½ gallons of iron liquor at 12° Tw.; heat to 212°, and leave to steep—12 lb. green copperas—3 lb. orpiment; grind all together perfectly, and add 1 gallon iron liquor

at 12°—4 lb. gum Barbary or Senegal ; grind all together. For darkest colour and standard add 4 gallons of iron liquor at 12° thickened with 16 lb. gum. Reduce for lighter shades with iron liquor at 12° thickened with gum.

No. 150.—China Blue for Block or Plate.—Persoz.

1 gallon water—1 quart honey—10 oz. powdered indigo—10 oz. green copperas—14 oz. starch.

No. 151.—China Blue for Roller.—Persoz.

$3\frac{3}{4}$ lb. indigo finely ground up with 1 gallon water ; add $3\frac{3}{4}$ lb. sulphate of iron dissolved in 1 gallon of vinegar, and thickened with 8 to 9 lb. of gum Senegal.

No. 152.—China Blue.—Persoz.

8 lb. indigo— $2\frac{1}{2}$ gallons water—8 lb. sulphate of iron—15 lb. gum arabic ; the whole well ground up together.

No. 153.—Fast or Precipitated Blue, Dark.

Prepare oxide of tin by dissolving 5 lb. crystals of tin in $2\frac{1}{2}$ gallons of water, and precipitating by soda, collect upon a filter, wash and drain. Take $2\frac{1}{4}$ lb. finely ground indigo—5 lb. caustic potash— $3\frac{1}{2}$ lb. of the oxide of tin ; boil ten minutes in an iron vessel. Then add nitric acid, diluted with an equal volume of water, about $1\frac{1}{4}$ gallon, to neutralize the potash, thicken with 1 gallon gum Senegal. Fixed by passing in lime and water. From a French manuscript.

No. 154.—Fast Blue from Vat.

Make a vat with 24 lb. lime, 18 lb. green copperas, 4 lb. ground indigo, and sufficient water. When the indigo is dissolved, draw off the clear and precipitate by a mixture of 20 lb. hydrochloric acid and 10 lb. crystals of tin ; collect and drain the precipitate upon a filter. Colour is made from $1\frac{1}{2}$ gallon of the precipitate, $2\frac{1}{2}$ gallons of gum water, and 4 oz. crystals of tin. From a French-Russian source.

No. 155.—Fast Blue for Raising in Soda.

Six quarts caustic potash at 30° Tw.—3 quarts water—4 lb. ground indigo—4 lb. granulated tin ; boil for six hours, supplying the waste from evaporation. The colour is made

by taking 3 quarts of the solution, adding 1 quart muriate of tin at 120° , and thickening with 6 quarts gum water. From an anonymous collection of receipts.

No. 156.—Fast, or Precipitate Blue.

1 gallon caustic potash at 20° Tw.— $1\frac{1}{2}$ lb. indigo— $1\frac{1}{4}$ lb. crystals of tin— $\frac{1}{2}$ gallon water—boil down to 1 gallon, and add 2 gallons thick gum water— $\frac{1}{2}$ gallon muriate of tin at 120° —1 quart muriatic acid. From an English receipt in manuscript. Not very good. It is preferable for fine colours to precipitate the deoxidized indigo, and drain the pulp as given in several receipts.

No. 157.—Precipitated Blue for Fast Blue.

$2\frac{1}{2}$ quarts indigo pulp at 4 lb. indigo per gallon— $2\frac{1}{2}$ lb. crystals of tin—2 gallons caustic potash at 40° Tw.; bring to the boil in thirty minutes; empty, and add $1\frac{1}{2}$ gallons boiling water; let stand all night; pour off the clear into 6 gallons cold water containing 1 lb. brown sugar, and precipitate with 3 pints of sulphuric acid diluted with 1 gallon of water, or an equivalent quantity of hydrochloric acid, so that the liquor is slightly acid to testpaper; filter, and drain the pulp to 2 gallons.

To make the darkest shade of blue, thicken the pulp with powdered gum Senegal about 3 lb. per gallon of pulp.

No. 158.—Green from Precipitated Blue.

Take 1 gallon of the precipitate No. 157; thicken with $3\frac{1}{2}$ lb. powdered gum, and add 14 oz. nitrate of lead and 14 oz. acetate of lead; stir well to dissolve. After fixing the blue, and washing, chrome to bring up the green.

No. 159.—Orpiment, or Pencil Blue, 1746.

Water, $1\frac{3}{4}$ gallons—potash, $3\frac{1}{2}$ lb.—quick lime, $1\frac{1}{2}$ lb.—indigo, $1\frac{1}{4}$ lb.—gum, 6 lb.—orpiment, $1\frac{1}{4}$ lb.; make the potash caustic by the lime and water, and let it settle clear; grind the indigo with the clear; heat and dissolve in the orpiment; then thicken with the gum. This is the oldest receipt I am acquainted with for this colour. It is taken from Dollfus-Ausset's account of Rhyiner's manuscript.

No. 160.—Orpiment, or Gas Blue, 1847.

1 lb. indigo—1 lb. orpiment—1 gallon caustic potash at 26° Tw.; boil together for half-an-hour in an iron pan, and thicken with 2½ lb. gum Senegal. This was one of the colours used in Woodcroft's gas blue process. A darker blue has 2 lb. each of indigo and orpiment, and a gallon of caustic potash at 36° Tw.

No. 161.—Soluble Tin Blue.

1 lb. indigo—2 lb. granulated tin—1 gallon caustic potash at 30°; boil for two hours; decant, and thicken with 2½ lb. gum. From an English manuscript. Used for a gas blue by Woodcroft's patent.

No. 162.—Grape Sugar Soluble Blue.

1 lb. grape sugar—1 lb. indigo—1 gallon caustic potash at 26° Tw.; heat to 120° F., and let stand a few days in a warm place until dissolved and decolourized; thicken with 2½ lb. gum. This was also used as a gas blue.

No. 163.—Lime and Copperas Vat for Woollen.—Grisson.

For 1,200 gallons of water—34 lb. quick lime—22 lb. green copperas—12 lb. ground indigo—4 quarts caustic potash at 34°. To be worked at a temperature of 70° to 80° F.

No. 164.—Bran and Madder Vat for Woollen.—Dumas.

For 500 gallons water—20 lb. indigo—30 lb. potashes—9 lb. bran—9 lb. madder. Mixed together hot, and let cool down to 90° F. The indigo is reduced by fermentation.

No. 165.—Bran and Molasses Vat.—German.

2,000 gallons water at 130° F.—20 lb. crystals of soda—2½ pecks of bran—12 lb. of indigo—6 lb. molasses; when the fermentation has reduced the indigo it is checked by addition of lime. See the present number of the "Textile Colourist" for details of a similar vat by Vinant.

No. 166.—Indigo Vat, cold, for Calico.—Persoz.

1,000 gallons water—50 lb. ground indigo—40 lb. to 50 lb. green copperas—50 lb. quick lime.

No. 167.—Indigo Vat, cold, for Calico.

60 lb. green copperas—36 lb. ground indigo—80 lb. to

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90 lb. of dry hydrate of lime. Rectangular vat, 6 feet 6 inches long, 3 feet 6 inches wide, 6 feet 6 inches deep, containing at working height about 900 gallons of water. English manuscript, 1850.

No. 168.—Indigo Vat, for Neutral or Lapis Style.

108 lb. of green copperas—36 lb. best indigo—108 lb. lime. Round vat, Continental style, 11 feet 8 inches deep, 6 feet top diameter. Two dips each about $2\frac{1}{2}$ minutes, sufficient for the shade of blue required.

[To be continued.]

7. Abridgments of Complete Specifications of Patents Recently Published.

A.D. 1875, September 7.—No. 3141.

COPLEY, JAMES, and JENNINGS, WILLIAM. (*Provisional Protection only*). "Improvements in Machinery for Dyeing, Scouring, Bleaching, etc." The improvement "consists of a cage inside the kier capable of partial or complete revolution as may be found most convenient. The axis of this is a perforated metallic tube passing at the top of the kier through a stuffing box and rotating at the bottom on a cone, through which superheated steam is admitted, and the steam passes through the perforated axis into the centre of the mass of the goods in the cage. The bars of the cage are perforated tubes connected with the axis from which superheated steam issues." "We obtain a vacuum in the kier by the condensation of the superheated steam, which vacuum draws solutions of soda, soap, chloride of lime, and other scouring, bleaching, and dyeing solutions from tanks connected to the kier by pipes fitted with stop cocks." "The apparatus may be made to work horizontally or vertically."

A.D. 1875, September 23.—No. 3319.

REID, WILLIAM. "Improvements in Apparatus to be used in

connection with various processes of treating Yarns with Liquids." The object of this invention is for contrivances, "so that yarns may be subjected to less handling and less risk of injury than in existing apparatus for the same purpose." The inventor in his provisional specification aimed at an arrangement of rods or poles on chains; holding the hanks of yarns which should carry them through the various "vats, "tanks, boilers, or other vessels containing the bleaching, "preparing, mordanting, dyeing, clearing, or other liquids with "which the yarns are to be treated." "And further of leading the yarns between pairs of wringing or squeezing "rollers to express the liquid, and one of each pair of such "rollers is made with a groove or depression to allow of the "passage of the rod or pole between the rollers." In the complete specification the inventor gives up the idea of conveying the rods or poles through the dyeing vats or vessels, and disclaims that part of his provisional specification and apparently confines himself to the squeezing, he says: "Hitherto yarns treated with liquids have generally had the liquid run from them by the well known twisting process in which they are not only handled to an undesirable extent, but are also very severely strained against each other and often injured." "No convenient plan has, however, been proposed or tried prior to my present invention, under which I accomplish the desired object by leading the yarns between the squeezing rollers by means of the rods or poles carrying the yarns, which rods or poles are themselves carried by endless chains, each rod or pole being enabled to pass through between the rollers with the yarn on it by forming a slight indentation in the surface of one or both rollers, and by arranging the movements so that each rod or pole enters the indentation provided for it in the roller surface."

A.D. 1875, September 23.—No. 3320.

WEIGEL, ALFRED. "Improvements in the Production of certain Colouring Matters." This invention relates to the production of certain colouring matters, soluble in water and suitable for dyeing, from a combination of sulphur with acetates or equivalent salts. "For example, I employ acetate

of soda, which I first render anhydrous, and then mix with sulphur. I subject the mixture to an elevated temperature, as for instance a red heat in a close vessel from which air is excluded. I thus produce a colouring matter which can be dissolved in water and employed for dyeing or like purposes." Other acetates can also be employed, and other non-metallic elements than sulphur, as iodine, phosphorous, and the like.

A.D. 1875, September 23.—No. 3328.

KNOWLES, SAMUEL, and KAY, JAMES. "Improvements in Apparatus for Drying, Stretching, Steaming, and Ageing Woven Fabrics." The claim of the inventors are, first, "for steaming and ageing printed fabrics by the action of steam and air combined, and the apparatus for performing the same;" secondly, "the application of rollers with expanding ribs to the drying apparatus in the Patent" (No. 3636, dated October 22nd, 1874) "whereby the fabrics are dried and stretched simultaneously;" and, thirdly, the application of the apparatus to other fibrous materials.

As far as the drying is concerned the improvement "consists in applying rollers with expanding ribs to increase the width of the fabric passing through the drying chamber," and "a small roller near each expanding roller to prevent the fabric shrinking back again." The steaming and ageing improvements upon the previous patent consist in modifications of the method of supplying heated air and steam to the chamber. The air is heated by being made to pass in contact with a range of steam chests in a lower chamber, whence it passes into the ageing room through proper openings. To supply steam there is a steam box on the under side of the apparatus, separated from the hot air chamber by a perforated plate; the steam is admitted into this box by side pipes, and passing through the perforations mixes with the air, and is forced or drawn by means of a fan under and over the steam chests, and then into the chamber through which the goods are to be passed.

A.D. 1875, September 28.—No. 3379.

FERGUSON, ROBERT. "Improvements in Machinery or

Apparatus for Applying Size and Colour to Yarns or Threads." "The invention is applicable to the ordinary machines now in use for polishing yarns or threads, and it consists in applying the size or colouring matter to the hanks of yarns or threads when distended on the ordinary stretching rollers, by means of a roller or brush revolving in a trough containing the size or colouring matter, or the size or colouring matter may be supplied to the revolving roller, which deposits it on the yarns or threads." The arrangements for carrying out the invention are described and illustrated by a drawing.

A.D. 1875, October 2.—No. 3425.

BRETNALL, SAMUEL, and RAWORTH, JOHN SMITH. "Improvements in Machines for Beetling and Finishing Textile Fabrics." The beetling is performed upon folds of the cloth passing under the beetles from a set of rollers at one end of the machine to a corresponding set at the other end, "the fallers acting upon as many folds of cloth at one time as there are rollers at one end of the machine." Several additions are mentioned. The rollers may be either hot or cold, nipped together by screws or weights, and driven by gearing at a uniform velocity which can be regulated according to the finish required. The cloth is finally taken up on cloth beams driven by friction at a higher surface speed than that of the rollers, so that the pieces are wrapped tight. Underneath each row of fallers a separate steam chest is placed, which can be heated or left cool as desired. "The fallers we use are much less in size than those common in the trade; we make them of timber, with an india-rubber or leather snug or projection, bolted on one or both sides for the slotted cross head to strike against.

A.D. 1875, October 7.—No. 3483.

JOHNSON, JOHN HENRY. "Improvements in Printing Textile Fabrics." (*A communication from Le Tellier and Verstraet, of Paris.*) This invention refers to the bowls or pressure cylinders in printing machines, and consists in the application of india-rubber as an elastic covering for such cylinders in substitution for lapping and blankets. For some interesting

reports upon this see the "Textile Colourist" for June, vol. i, p. 374. The language of the specification, in describing the advantages of the improvement, is obscure, and not very intelligible.

A.D. 1875, October 9.—No. 3512.

BURLISON, ROBERT, and WHITAKER, JAMES. "Improvements in Tentering and Drying Machines." This patent refers to stretching and drying textile fabrics, that is, drying only from the moisture required for stretching, and doing away with tenter hooks. The machine is too complicated to be described apart from the drawings, but it may be said that the cloth to be treated is wound on a beam, from which it passes over stretching bars and rods, and then over a steam chest or box from which steam issues, then moistened by rollers and carried to the nipping rollers which stretch the fabric; the cloth then passes over a roller covered with wire card or holding pins, to prevent the fabrics from shrinking, and lastly on to a large steam cylinder to be dried.

A.D. 1875, October 9.—No. 3517.

HOLT, WILLIAM. "Apparatus for Steaming Textile Fabrics and Yarns or Warps." In this apparatus the goods to be steamed are wrapped or beamed upon a perforated cylinder, inside of which another cylinder is placed concentrically "so that steam may first be introduced to the inner cylinder, and pass through the perforations thereof to the outer cylinder, and thence through the perforation in the penphery thereof to the fabrics or warps which are to be warmed thereon. By this invention the pressure of the steam is reduced in passing through the first perforations without reducing its heat, and steam is thereby economised." The whole arrangement can be covered in by a steam-tight casing, and the steaming may be reversed by driving steam from the outer casing inwards.

A.D. 1875, October 14.—No. 3570.

SCHOFIELD, JOHN, and others. "Improvements in Means or Apparatus for Finishing Woven Fabrics." This invention consists in the employment of one or more perforated steam cylinders in combination with the usual washing or drying

apparatus. The said steam cylinders are capable of rotating in a suitable framework, and the fabric, after leaving the washing apparatus, is conducted by guide rollers round them, the guide rollers being arranged so that the fabric may embrace as much of the circumference of the cylinder as possible." The claim is for the combination of washing, steaming, and drying apparatus.

A.D. 1875, October 21.—No. 3655.

KENWORTHY, WILLIAM EDWARD. "Washing Woollen Yarns, Cotton Waste, etc." (*Provisional Protection only.*) The stuff to be washed is put into a vessel with the water or washing material, and a strong blast of air led amongst it by pipes or diaphragm, which causes an agitation and so washes and cleanses the material.

A.D. 1875, October 22.—No. 3669.

SMITH, THOMAS JAMES. "Improvements in Bleaching Wool and Silk." (*A communication from Du Motay.*) It is said that oxidizing agents alone are insufficient to bleach wool and silk, and this patent was for following the oxidation processes by treatments with sulphurous acid and bisulphites.

A.D. 1875, October 28.—No. 3746.

GODEFREY, LEON. "Process of Printing or Ornamenting Woollen or other similar Textile Fabrics." (*Provisional Protection only.*) The object was to give a new mixed appearance to fabrics; the process consists in first printing a granite, or other ground design, on one or both sides of an unbleached woollen or woollen and cotton fabric, fixing by steam, then fulling and dressing or finishing.

A.D. 1875, October 30th.—No. 3773.

PAGET, HARRIET SARAH. "Painting Designs upon China, Wood, Iron, Paper, Silk, Canvas, etc." The form of the object is cut out in india-rubber, and the colours applied by brush, and the india-rubber is then pressed upon the matter to be printed.

A.D. 1875, November 8th.—No. 3876.

WAY, JOHN THOMAS. "Improvements in the Manufacture of

Woollen and Silken Fabrics, and of Soap and Detergents for use in these Manufactures, and for other purposes." The patentee says—"I have found that compounds in which phosphoric acid is combined with alumina and soda, or potash, in proportion of single equivalents of the two former substances to three or four equivalents of the alkali respectively, have valuable detergent properties." "When any fatty, or greasy, or analogous substance is brought in contact with solutions of these salts, the alkali is given up, whilst, at the same time, the alumina combines with the phosphoric acid as phosphate of alumina. In these salts a larger proportion of the alkali is therefore available for detergent purposes than in the biphosphate of soda, which is the subject of former patents granted to me." To obtain a suitable material, caustic soda at 30° Tw. is saturated with alumina, and then rhombic phosphate of soda is added until the nitrate of silver test no longer shews a black or brown tinge of oxide of silver. The mass is then evaporated down until it sets on cooling. A method of employing native phosphate of alumina is described. "The salt obtained by either of these processes I employ in the manufacture of wool and silk. In the manufacture of wool I employ it in the various scourings to which the fibre or fabric is submitted in the process of manufacture, in lieu of soap or other detergent. In the manufacture of silk I employ the salt to remove the natural gum from the fibre." One part of the salt to 100 of water is a suitable quantity. It may be employed also in conjunction with ordinary soap.

A.D. 1875, November 9th.—No. 3889.

TATTERSFIELD, JAMES WALKER. "Improvements in Machinery or Apparatus for Finishing Woven Fabrics." (*Provisional Protection only.*) This related to the production of what is known as the "wave finish," and was for substituting mechanical means for the hand process. The cloth was to be drawn over rollers, and in contact with a series of rubbers consisting of strips of wood covered with india-rubber.

A.D. 1875, November 13th.—No. 3954.

FLETCHER, THOMAS. "Improvements in Apparatus employed

for Bleaching Cotton or other Fibrous Substances or Fabrics." This invention "consists of a certain construction and arrangement of the kier and its adjuncts, whereby the kier is made perfectly self-acting, and will work with either high or low-pressure steam." We cannot follow the patentee's description without a drawing to refer to, but the drawing may be described as a single kier with a puffer pipe. The peculiarities we observe in the kier are that the puffer pipe is continued below the false bottom, and "opens out into a funnel shape, beneath the centre of which, in the bottom of the kier, is the opening with which the high-pressure steam communicates." The "bonnet" for spreading the liquor from the puffer pipe is fixed on the kier tap, and there is "a valve for closing the top of the puffer pipe worked by a screwed spindle passing through a stuffing box in the cover of the kier." The kier being filled with goods, the working is commenced by opening the blow-off pipe, closing the top of the puffer-pipe by the valve, and turning in low-pressure steam from the top to blow through. When the blowing through is finished, the low pressure tap and the blow-off tap are closed, and the valve lifted from the top of the puffer pipe, the bleaching liquor is admitted, and the high-pressure steam turned on, while, at the same time, a small blow-off tap at the top of the kier is opened, but whether left open all the time of working or not the specification does not state. The claims are for a self-acting kier complete in one vessel, and the use of the valve closing the puffer pipe whilst blowing through.

A.D. 1875, November 16th.—No. 3979.

PATON, GEORGE. "Improvements in Dyeing and Dressing, or Sizing, and otherwise Preparing Warp Yarns." (*Provisional Protection only*). The improvements consist in combining the sizing and dyeing in one operation. The dyeing materials being mixed with the size, and the warps passed through and dried, and, if necessary, again passed through the same bath to obtain a satisfactory depth of colour.

8. British and Foreign Patents, from the Commissioners of Patents Journal, June 27th to July 21st, 1876, inclusive.

Colouring Matters.

1948. WILLIAM HENRY PERKIN, of Sudbury, in the county of Middlesex, for an invention of "Improvements in the manufacture of colouring matter suitable for dyeing and printing."—Dated 26th June, 1869.—The stamp duty of £100 has been paid upon this patent.
2534. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for the invention of "An improved black dye."—A communication to him from abroad by Charles Rave, of Paris, France.—Provisional protection has been granted.

The following are French Patents.

- 110,903. GUIMET, of Lyons, for "Purple and brown ultramarine."—Dated 6th January, 1876.
- 110,904. GUIMET, of Lyons, for "Green and yellow ultramarine."—Dated 6th January, 1876.
- 110,989. WOLFF and BETLEY, of Paris, for "Improvements in obtaining aniline dyes."—Dated 6th January, 1876.—(English Patent, 5th July, 1875.)
- 111,319. WOLFF and BETLEY, for "Improvements in the production of colouring matter for dyeing and printing."—Dated 1st February, 1876.
- 111,485. WOLFF and BETLEY, for "Improvements in the production of aniline dyes."—Dated 12th February, 1876.—(English Patent, 26th January, 1876.)
- 111,561. GRAWITZ, of Paris, for "Manufacturing a series of colours derived from alizarine and purpurine or direct from anthracene for dyeing and printing."—Dated 18th February, 1876.

Singeing, Bleaching of Cops, Jute, &c.

468. CHARLES TOUSSAINT, one of the firm of Toussaint, Levy, and Co., of Saint Dié, in the department of the Vosges, France,

Manufacturer, for an invention of "Improvements in bleaching cotton on shuttle cops, bobbins, or in hanks."—Dated 5th February, 1876.

2529. JOSEPH JULIUS SACHS, of Canada Government Building, King Street, Westminster, in the county of Middlesex, Manufacturer, for the invention of "Improvements in bleaching and preparing for dyeing or printing cotton, wool, hemp, flax, jute, and other fibrous materials."

The following are French Patents.

- 111,350. TOUSSAINT, LEVY, and Co., for "Processes and apparatus for bleaching cotton on cops, bobbins, and in skeins."—Dated 2nd February, 1876.
- 111,454. BAERLIN, for "Improvements in mordants, dyes, and size of threads."—Dated 12th February, 1876.
- 111,992. DUPETIT, Senr. and Junr., of Amiens, for "Singeing tissues of cotton and other tissues."—Dated 23rd March, 1876.

Dyeing and Printing Processes and Materials.

2190. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for an invention of "Improvements in machinery for printing oil-cloth or other fabrics."—A communication to him from abroad by W. H. Townsend, of New York city, United States of America.—Dated 23rd June, 1873.—The stamp duty of £50 has been paid upon this patent.
2314. HENRY BERNOULLI BARLOW, the younger, of Manchester, in the county of Lancaster, engineer, for an invention of "Improvements in machinery for washing and dyeing fibrous materials."—A communication to him from abroad by Charles Grandison Sargent, of Graniteville, Massachusetts, United States of America.—Dated 4th July, 1873.—This patent has become void.
269. OATES INGHAM, of the firm of Oates, Ingham, and Sons, of Bradford, in the county of York, Dyers and Finishers, and CHARLES HERBERT HOLT, of Huddersfield, in the same county, Engineer, for an invention of "A new or improved method of and apparatus for steaming or 'blowing' woven fabrics in the process of dyeing and finishing."—Dated 24th January, 1876.—This patent has passed the great seal.
2630. CHARLES THOMAS KINGZETT, of Shaftesbury Terrace,

Warwick Road, Kensington, Chemist, and MAXIMILLIAN ZINGLER, of Buckland Terrace, Belsize Park, Gentleman, both in the county of Middlesex, for an invention of "Improvements in the preparation of blood-albumen, and the application of the same for purposes of dyeing and printing on textile and other fabrics with colours also applicable to sizing and enamelling wood, glass, and metals."—Dated 26th June, 1876.—Notice to proceed has been given.

2661. RICHARD DIXON, of 79, Redcliffe Gardens, Kensington, in the county of Middlesex, Fur Merchant, for an invention of "Improvements in the manufacture, dressing, dyeing, and colouring of furs, skins, and animal and vegetable fibres of all kinds."—Dated 28th June, 1876.

2748. JAMES MORTON, Manager to Messieurs William Stirling and Sons, of Cordale and Dalquhurn, Turkey-red Works, in the county of Dumbarton, North Britain, for an invention of "Improvements in preparing woven fabrics and yarns of cotton or other vegetable fibres for being dyed or printed."—Dated 5th July, 1876.

8. W. BAERLEIN, of Manchester, for "A process of mordanting, dyeing, and sizing yarns.—2 years.—(Secret.)—Dated 26th February, 1876.—Austrian patent.

The following are French patents.

III,531. GAILLOT, of Lyons, for "Applying gold and silver on stuffs."—Dated 27th January, 1876.

III,568. LYEUTE, Sons, of Puteaux, for "A mechanical colour-tub for printing stuffs."—Dated 21st February, 1876.

III,652. ANDERSON and ROTHERHAM, for "Improvements in dyeing and finishing silks, cotton, &c."—Dated 25th February, 1876.—(English Patent, 2nd December, 1875.)

II2,001. KNIGHT, DU TEMPLE, and FARINAUX, of Lille, for "A process of dyeing with physical or chemical discharges, and a continuous rotary machine employed therefor."—Dated 3rd April, 1876.

Wool and Silk Treatments.

1646. JAMES MILLEN DICK, of Buffalo, in the county of Erie, in the state of New York, one of the United States of America, has given notice to proceed in respect of the invention of "Improved method and apparatus for removing moisture from wool and similar substances."

2505. EDWARD GRIFFITH BREWER, of Chancery Lane, London, for the invention of "Improvements in bleaching and purifying wool.—A communication to him from abroad by Messrs. Dandier, père et fils, of Paris, France.—Provisional protection has been granted.
2627. EDWARD DAVID ARTHUR MARRINER, Worsted Spinner, Greengate Mills, Keighley, in the county of York, and CHARLES HOYLE, Machine Maker, Market Street, Keighley, in the county aforesaid, for an invention of "Improvements in machinery for washing and drying wool or other fibrous substances."—Dated 26th June, 1876.
2916. EDWIN POWLEY ALEXANDER, of 14, Southampton Buildings, in the county of Middlesex, Consulting Engineer and Patent Agent, for an invention of "Improvements in the treatment of woollen and silk fabrics and other goods composed of animal products with a view to the removal of any vegetable substances contained therein; also in the apparatus or means employed therefor."—A communication to him from abroad by Daniel Michel, of Paris, in the republic of France, Woollen Waste Manufacturer.—Dated 17th July, 1876.
2947. CHRISTOPHER WEBB SMITH, of Barnwood, near the city of Gloucester, Chemist, for an invention of "Improvements in and apparatus for scouring or cleansing woollen cloth, yarns, and wastes, and in recovering valuable products from the materials which have been used in conducting the said scouring or cleansing."—Dated 19th July, 1876.
- 173,762. LOUIS R. BROADBENT and CHARLES F. BROADBENT, of Baltimore, Md., for "Processes for separating woollen from cotton fiber."—Application filed 8th February, 1876.—American patent.
- Claim.*—"The within-described process of separating wool from cotton fiber, which process consists in steeping the fabric in water, then boiling it in hydrochloric-acid solution of a specific gravity of from 1.015 to 1.19 for from three to twenty-five minutes, and withdrawing, substantially as described."
- 39,677. A. DE SOURDEVAL, for an imported invention of "Scouring greasy wool, &c."—Dated 31st May, 1876.—(French patent, 10th May, 1876.)—Belgian patent.

The following are French Patents.

- 111,331. HAMMELRATH, for "Scouring wool."—Dated 2nd February, 1876.

- 111,352. WAY and JONES, for "Detergents for washing wool and silk, and for other purposes."—Dated 3rd February, 1876.—(English patent, 5th August, 1875.)
- 111,830. LECLERQ, for "A chemical mechanical process of cleansing and disacidifying wool and other textiles containing vegetable substances in suspension."—Dated 21st March, 1876.

Finishing Processes.

1918. ANTOINE JULIEN DEBLON, of Fives-les-Lille, in the Department of Le Nord, in the French empire, Manufacturer, for an invention of "Improvements in machines for callendering stuffs."—Dated 23rd June, 1869.—This patent has become void.
242. GEORGE HENRY NUSSEY and WILLIAM BRADSHAW LEACHMAN, both of Leeds, in the county of York, for an invention of "Improvements in machinery or apparatus for pressing woollen and other woven or felted fabrics."—Dated 21st January, 1876.—This patent has passed the great seal.
2956. JOSEPH KEIM, of Tharm Alsace, Allemagne, for an invention of "Improvements in machinery for stretching and drying textile fabrics."—Dated 20th July, 1876.
- 174,308. CHAS. E. SCRIMGEOUR, of Almonte, Canada, Assignor to the Rosamond Woolen Company, of the same place, for "Finishing cloth."—Application filed 19th November, 1875.—American Patent.
- Brief.*—"Steam is passed through a tank of water before passing to the perforated distributor, by which its surplus heat is removed, and it more readily is deposited in condensation in the cloth."
- Claim.*—"The combination of close tank A, to be partially filled with water, an induction-pipe B, connected with the steam space of a boiler, and extending into the tank below the water-line, the eduction pipe C, and the perforated cylinder D in box E, as and for the purpose specified."
- 39,692. J. NICODEME, of Anseremine-Dinant, for "An apparatus for measuring tissues."—Dated 1st June, 1876.—Belgian patent.

The following are French Patents.

- 111,453. ALLARD, for "A machine for dressing velvet and other similar tissues."—Dated 16th February, 1876.
- 111,780. THOMAS and DUMOLLARD, for "Decorative finish of light tissues."—Dated 25th March, 1876.
- 112,050. BOIRIVAUT, of Lyons, for "A machine for drying dyed silk, wool, linen, and other threads."—Dated 1st April, 1876.

THE TEXTILE COLOURIST.

No. 9.]

SEPTEMBER, 1876.

[Vol. II.

I. *Materials for a History of Textile Colouring, No. 3.*

IN this article we give an account of the contents of a book published with the following title:—"THE BRITISH *Manufacturers Companion*, AND CALICO PRINTERS ASSISTANT; BEING A TREATISE on CALICO PRINTING, *in all its Branches, Theoretical and Practical*; WITH AN ESSAY on *Genius, Invention, and Designing*; RULES FOR Drawing, Cutting, Printing, Engraving, Colour-making, Bleaching, &c. Suggestions for the Advantage of Manufactures; And many valuable Hints to the Proprietors of Print-fields. BY CHARLES OBRIEN, *Callico Printer*. LONDON: PRINTED FOR THE AUTHOR; AND SOLD BY HAMILTON AND CO., AT THE BUST OF SHAKESPEARE, BEECH-ST., NEAR FINSBURY SQUARE; AND VERNON AND HOOD, BIRCHIN LANE, CORNHILL. (1790)."

This book, though not one of those which can be called rare, is naturally from its date and subject somewhat scarce, and not generally accessible to those now in the author's trade, it has moreover a special interest as being the first work on calico printing published in England, and as far as the author knew, and as far as we ourselves know, the earliest book in any language especially devoted to printing on textile fabrics in which any attempt is made to go into a detailed account of the operations. The subject is therefore treated in an original manner, and almost entirely from the author's practical knowledge and experience of the business, and it

may be said that in those subjects with which the author was most perfectly acquainted, namely, designing or pattern drawing, putting on, pinning, block cutting, engraving, and printing, there has been no book since which goes into equal detail, or treats the subject in so minute and practical a manner. In what may be called the chemical department of the subject the treatment is less satisfactory and more superficial, either from a want of knowledge or familiarity with this part of the business; or because the writer was restrained by prudential considerations from communicating all he knew upon what was generally considered the mysterious and secret part of the business. It is, however, clear that O'Brien had an intelligent knowledge of what was contained in the then recent works upon chemistry, for he frequently refers to contemporary writers of the more scientific class, and quotes Hellot and D'Alpigny on Dyeing, Berthollet, Lewis' Notes on Neuman's Chemistry, Priestley, Percival, Macquer, Fourcroy, the Manchester Memoirs, Dr. Home, and other authorities.

The work is in small octavo; there is no index, and it is not paged, but contains about four hundred pages, with one copper plate referring to block making. Of the two copies now before us, one has a long introduction which in the other has been cut down to three pages. The title page is also quite different, and bears the date of 1792, while the other has no printed date, but a pencil inscription that it was published in 1790. The remainder of the contents of the two volumes appear to be identical in every respect.

From internal evidence it appears that the author of this work was at one time a designer, and probably before that a putter-on, or actually a block cutter, and in the course of his experience picked up a respectable knowledge of calico printing as it existed eighty or ninety years ago in England. There is not a formal receipt in the whole book, and practical processes are referred to in an obscure, half mysterious manner, as if the writer desired to impress the reader with the idea that he could say a good deal more about them if he chose, but that he is only writing for adepts who can understand what he hints at. We propose to go through the book,

giving such extracts as are of interest in shewing what was the state of knowledge at the writer's time, and what the ideas of an original and not unintelligent observer were upon various proceedings both inside and outside of the print-works. The first subject treated of is pattern drawing, and commences with some definitions of the qualities required in the pattern drawer or designer, the two terms being synonymous, while the term drawer is applied to one who draws the pattern on the block for the cutter. A designer should possess "fertility of invention, with judgment to adapt that fertility to the best purpose as regards taste, effect, execution, and expense." This definition of an original mind is however immediately lowered by the author continuing that the designer should be "at least, one who can improve on what is doing by others, or can readily catch the reigning style, and by adopting it, form his designs accordingly."

"It may, nevertheless, be observed (making a transition from Pattern Drawing to the Patterns themselves) that it is difficult to say, what really constitutes a good pattern, as decisions on that subject are formed by different persons from very different motives. For instance, a Draper's determination of one is biassed by what will best suit his line of trade; a Printer's, that which is adapted to produce the desired effect at the least expense; while a buyer's opinion is guided by what is most generally exhibited in the shops; and many patterns acquire the character of being good ones, merely from a Draper having it in his power to command a general display of them under every advantage; for the most fanciful and best executed pattern would have little chance of selling well if seen but in a few places, or the sale not otherwise forwarded, as it then would not have the appearance of a generally approved one, and consequently it would be disregarded in a proportionate degree. But as this will be occasionally considered in other places, a few sentiments respecting GENIUS, FANCY, and INVENTION, as more immediately the subject of this section, will now be offered."

We do not think our readers would be in the least interested or find any profit in Mr. O'Brien's dissertation upon Genius, Fancy, and Invention, which as he himself says "leads into

such metaphysical obscurity or perplexity, that the most intelligent are at a loss how to satisfy such enquiries." But in fact the author does not long soar in the higher regions of speculation, soon coming down to eminently practical details in connection with designs and designers, as when arguing against the desire to make designers out of any youth, he says, "unless a lad is likely to shew those faculties which will get him through life with credit and ease as an artist (in which class designers may be included) he had better be put to any common mechanical employment, as certainly nothing can be a greater misery to a man, than to think his living depends upon the productions of fancy and he is unfortunate enough not to possess a single ray of it, and that, consequently, his utmost exertions are despicable and of course not worth exhibiting." The following extract seems worth reproducing as containing some very just observations, although not so applicable at this day as when first written; for designing for calico printing has come down in a great measure from the position of an artistic occupation to a merely industrial one, and has felt like other trades the effects of the minute division of labour.

"A designer ought not by any means to be considered in so mechanical a light, as if fancy or invention were of such a nature that he can at all times command a successful operation (those are particularly alluded to here who are engaged as designers to work a stated number of hours in a day; but to treat designers with proper address is what few principals are competent to), similar to a person performing a merely mechanical piece of work, in which little more than utensils are needful, and the subject to be acted upon is immediately and conveniently at hand. To illustrate which it may be observed, that Principals themselves affect to say: Designers should only work when so disposed, yet many of them, inconsistently with such a position, think nothing done unless they see something on paper; making hardly any account of what the Invention is at work upon; but contrary to this practice, it is here said that the designer should not be asked, except on singular occasions, how he means to do such a part? what will be put in this or that place?

what will be the colour of this object ? and so on ; but that a proper mode is (when not left to work entirely from his own fancy) for him to be told what sort of patterns is wanted ; on which accordingly he draws a number slightly, or perhaps nearly perfect, agreeably to the nature of them ; from these a selection is made as having the best effect ; afterwards another is made, including that quality with their adaptation for working ; and even from these it may be needful to make a selection as proper to shew, or to be put into execution.

. A designer can do little with pleasure to himself at a Printing-ground, if under restraint, or subject to that kind of control, or enquiry, which has been expressed above ; or if his employer be of that cast who consider all under them as but mere machines to procure themselves profit, and that as such they have nothing to do but to spur everyone on by any method, however coarse and unfeeling. One person only is proper to give orders (no matter how many have been previously advised with) for rarely do two or more agree in opinion ; and for a designer or any other to receive orders from several, and these orders different or counter-manding, no one need be informed is productive of much embarrassment, and often subversive of what each party desires."

The following extract shews the desire which existed for novelty of design in these days ; the term Draper in constant use may be considered equivalent to that of Warehouseman at the present day ; the print trade at this date was, of course, in its infancy, and the production very limited ; machinery for printing had only just been invented and scarcely put into use ; the greater part of the trade was still in the neighbourhood of London, and hardly anything was printed for exportation.

"It often happens, too, that many (Drapers particularly) are violent in requiring something new, or totally different from what has ever been seen ; all this has a busy sound, and in idea promises a great deal, or at least implies the hope of a great deal ; but could it be procured, the expectation might not be answered, as it generally seems that when anything happens to be produced, very different from the common run or appearance of work, or what may be called the reigning style, it has not the chance of getting into vogue,

for reasons already given, except when a Draper of eminence, who holds his connections as it were by a bridle, is determined to push what is a favourite of his, though even that will not always succeed ; for somehow or other capital blunders are now and then made by the most experienced in the choosing of patterns. Cautious Drapers are, however, not very forward in this respect ; they know, indeed all must, there are certain classes of patterns that ensure sale, yet a continuation of one style will tire in time, and the utmost efforts to continue it will not always be propitious, for innovations in style rarely happen abruptly ; they are brought about by slow degrees, or, in fact, more by accident than design, and oftentimes in a manner contrary to what any one might conceive. Much, to be sure, is sometimes said of the fickleness and whimsicalness of Drapers and others, but there surely is little cause, it being natural to be tired of anything ever so excellent when very familiar, and of course novel or different appearances are sought after."

After a good deal of sound common sense upon the way in which designs are produced for the trade, and the claims and real merits of designers are discussed, we are told that "an engaged designer at a Printing-ground is now little more than a compiler," and that those designers who had credit for originality were frequently short of flexibility and let the times go by them ; how in questioning the very existence of genius or inspiration in most designs, the author candidly confesses that "he himself, as a designer, is more put to his shifts than he at all times chooses to own," and somewhat solemnly warns those designers who claim the gift of genius—

"To be cautious how far they give themselves praise or credit for what they do possess, as rarely half what a person advances of himself is believed ; and in this case designers as well as others, whose existence depends on public caprice, would be less arrogant or puffed up in the zenith of their reputation if they frequently reflected on the versatility of taste and fashion, not knowing how soon such caprice or mutability may affect them, as it is not every one that can readily come into every turn of that fickle despot. That this has been the case is well known in instances of several who have

been deemed capital Drawers but are now almost totally disregarded; hence, if the writer may venture to advise in this point, let every Designer who wishes to secure his credit as long as possible, not foolishly affect to stand alone, or obstinately to oppose or condemn that style which is prevalent, but gradually slide into the changes as they happen, or blend them with his own peculiar manner; otherwise, certain it must be, that from the fickleness of opinion or fancy, and the consequential change of fashion, together with the probability of a rising generation of designers eclipsing him, he at a certain period will regret that self-sufficiency which blinded him to natural defects, or that restlessness which stifled what prudence ought to have suggested."

The foregoing extracts illustrate very well the style of this early writer upon calico printing, and shew that he neither wanted sense nor facility of expression. Of his hints upon designing many of them are so technical as not to be of general interest, and they naturally refer to a taste and to styles long since disappeared, but here and there some small insight is got into the ways in which business was carried on, and the kind of work done by printers. Of the extreme minuteness of the instructions given, the following is an instance; he is speaking of a prevailing taste which required a plain white object to stand forward in the design.

"This enlivening effect is generally destroyed in dark patterns, where the colour ends in shades within an object, or without being bounded by a line of some sort, as it gives the white about it a tinge, and in woalded work,* the less the yellow touches or goes over the black the better, as it generally hurts and renders it of an olive hue. This, however, depends upon the colour, but more particularly so when executed without grassing or fielding, as in the case of patterns brought up in sumac and bran-bleached, the cloth not being then of a good white.

In drawing some classes of patterns it is as well to make them as general as possible, though that it is granted, is rather an after consideration; and in patterns that are to have chemical or loose

* So spelled; prints which were dyed partly with weld, a now almost unknown yellow dyestuff.—*Ed.*

colours thrown in, which soon fly off, there should be fast colours (unless the whole is in chemic) under them, or so connected that there may seem as little deficiency as possible when such loose colours disappear."

In the rules for putting the pattern on the block, the writer enters into detail upon the kind of wood proper for different patterns; if the pattern is close and small, nice in the joinings, and will require smart knocking with the maul, crossed oak backs are to be preferred, and a clear whole face; but if less nice in the joinings larger blocks with joined faces may do, and light patterns which do not need much knocking will do with deal backs. In coarse cutting, without hatting, soft wood is preferable to hard, though the soft wood may need hatting the boundage may be much larger. In some instances, where solids are wanted to furnish, and they are not very large indeed, sycamore or some other spungy wood is best. With regard to the grain of the wood, the reader is told that it should not usually correspond with the direction of the fine lines in the pattern, as then they will not stand well, especially if they have a slender bottom; but a block should be selected having a wavy or curly grain; fine lines should not however be cut across the grain. Amongst the instructions to the putter-on, he is told "to consider where the drawing may be altered, or what may be left out in the cutting or eased in the pencilling, or in other words, how it may be executed with the greatest ease and least expense." In a foot note he adds, "this may not please some cutters, (*i.e.*, lessening the expense) but the writer makes equally free with masters, as will appear."

These instructions are continued with equal minuteness for many pages, not the most trivial point in any respect seems to have been overlooked, and as we read we are astonished, not that the writer should have known all these details, for a long practical acquaintance with the business would give that knowledge, but rather that a practical man should have had the patience and the method to accurately note down and arrange his observations in so thoroughly exhaustive a manner. Not only is the smallest detail of manipulation fully treated of, but not unfrequent reference is made to faults from bad

workmanship which may arise, or defects which may turn up in a finished block from actual bad faith on the part of the cutter from having a pique against the putter on, or *vice versa*, or ill will against his employer, and instructions are given how to take such proofs of the preliminary work as to shew where the real blame must be laid. Such measures of protection were not uncalled for in the days of block printing when elaborate workmanship was required, for in some instances wired blocks given out to the block cutter were so large and difficult that from thirty to forty days' skilled labour were allowed for their completion, and were consequently very costly implements in printing; add to this that if the block was not fit to print with, or inferior, great loss fell upon the employer, whose goods must either go into the market imperfect or he must disappoint or break faith with his customers whom he had engaged to supply with certain patterns. From Mr. O'Brien's book we gather that the proper amount to pay for cutting blocks given out to those working at home was a disagreeable and troublesome question for principals, and left much room for sharp practice on the part of the tradesman, so few were able at once to know what was a fair price to give for the cutting of a certain block, and so few able to judge if it had been well and honestly done before it got into work, that much unpleasantness arose between the employers and employed. It is observed that the best block cutters worked at home, and this is accounted for on the ground that if employed on the printworks they had not the freedom of following their own methods, and were annoyed by too much overlooking and interference on the part of the masters, who, it would appear, insisted upon close and regular attention to work. O'Brien, who in this takes the part of the block cutter, says that those men who are superior in this branch are not always alike able or disposed to work, and that it would be more advisable to form an estimate of a man's abilities from his production in a day, a week, or a month, then from his working in a mechanical sort of way.

It may be mentioned that we have used the word block as

we believe it is universally used in England at this day to signify the cut block used by the block printer, but in this treatise the word is only used to indicate the wood prepared for putting the pattern on; after cutting it is called either *the print* or *the ground*, the former when it contains the sprig or parts of it, and the latter when it has the ground design on which was in the great majority of cases printed after the sprig had been dyed.

In the section on printing, the writer deems it necessary to dispute at some length the truth of a maxim held by the printers, that no one but a practical printer has any right to attempt to direct, criticise, or examine their work; he does not dispute that if other things were equal, a printer is the fittest person to direct a printshop, but insists on the other hand that "a mere printer knows no more about calico printing properly so called than a common field man, and that unless a printer has a general judgment of whatever has any relation to printing in all its branches, he is not so proper to superintend as another who possesses such a portion of judgment, although he never had a print in his hand." We do not follow the instructions to printers, but think it will be of interest to insert a couple of extracts concerning what is called inattention in printing and its results in some cases.

"The writer once observing that about one of the corners of every print that was laid the impression was heaviest, in pointing it out he could get no other reply but that the print worked fuller there than any other part; this, however, from the appearance of the face, he would not grant, the printer still insisting it was so, till at last looking obliquely on the sieve, as the tearer worked, he saw a ridge of colour left nearly in one place after the last stroke, which the tearer could not rectify; at length, looking at the brush, it was plain that one part by some means had been burned so considerably, that the hairs were so shortened and thinned, that that part hardly touched the sieve, and from her method of holding it a ridge of colour was always left, that caused the effect above mentioned. Now here was a triple instance of inattention; in the first place the tearer had carelessly suffered the brush to be burned in drying it (as she afterwards owned,

and probably fear of being reprimanded induced her to keep it secret), in the next place she did not perceive the effect it had on the sieve, and lastly, the printer, if he perceived the effect on the table, did not, as he should have done, see that his apparatus (which included the tearing brush) was or was not in proper order.

Another time the writer seeing the head of the impression in general fuller than the rest, he of course mentioned it; but here the fault could not be discovered to be in the tearing, nor did it appear to be in the face of the print, and the Printer was sure it was not his fault, for he dipped and turned his print and then dipped again (the print requiring much colour), but at last he was convinced it was from his knocking it, and yet perhaps he was not to blame, for in the middle of the back that was let in there was a very hard knot, and the other part towards the head remarkably soft, so that by insensible degrees the knot had at length, by its resistance to the blow of the maul, caused it to slide as it were into the soft part, where it had evidently made a cavity, and the Printer as insensibly giving into that direction of the maul, at length instead of hitting the back in the middle, hit it nearer the head, which made the impression heaviest in that part."

We pass over two or three other instances, given by the writer, of faults arising from the printing, to refer to the account of one which is not without a touch of that severe comicality which foremen sometimes practise on their subordinates when they fall into their hands. The printer had to work a pattern of sprigs that stood 6 or 7 inches apart, and managed it so that the off edge of the piece divided the sprig, which therefore fell half off and half on the cloth, so that in making it up into a garment either 3 inches must be cut to waste or half a sprig appear, which fault could have been easily avoided.

"Thus the garment could not be made up without imperfect sprigs or without cutting to waste; now in this case it may be observed there wanted an attention to the remotest circumstance, that of the wear, or at least the making up of the garment, and this includes a query which might with propriety have been put to that printer, which is, If he had been printing that piece as a present for a

favourite female, whether he would not have bestowed a little more consideration on the particular alluded to?"

The writer is very brief in his remarks upon pencilling, as he seems to think it quite hopeless to expect that English pencillers can do anything better than filling an outline with colour. In foreign patterns he says a deal of work is done by the pencil, but the attempts which were made in England to give pin outlines as a guide for shapes to be made by the pencillers resulted in rough inaccurate work which did no credit to the design, except in pencilling light shades where the dark pin outlines catch the eye, and take off the attention from the inaccuracy or bad shape of the pencilling.

In the section upon engraving reference is made to engraving by the graver and the punch only, and that only for the flat press. In this part of the work there is not the least reference to engraved rollers, or roller printing in any way.

The writer next proceeds to the processes which, in the olden time of printing, were distinguished as the out-door part of calico printing, they being generally carried on in open sheds or in the open air; they include in our author's words, copper-work, fielding, and colour making. Copper-work it must be explained at once means work done in copper boilers, *i.e.*, bleaching, dunging, and dyeing. Bleaching, or as it was then commonly called preparation, is treated of by our author, though it was a separate business; the term "bleaching" was used by the calico printers for the whitening of the unprinted parts of goods by spreading them on the grass after printing and dyeing, and also in those few cases where the goods sent to be printed were not deemed sufficiently white. We note in this part of the work that the rot steep, where fermentation is promoted by mixing rye-meal, bran, etc., with the steeping water is spoken of unfavourably, and it is recommended to simply steep the goods a night, or longer, in common water; the use of lime is referred to, and from the language we should say that Dr. Home's work on bleaching was consulted by the writer. It is remarked that some articles manufactured in India, and brought over unbleached, cannot be made white here. May dew quickly whitens cloth, and it is

observed that immense numbers of insects are formed on the substance left after evaporation. The use of ashing is to take out greasy matters which would prevent the "striking of the colour" in the "maddering." The circumstance of skinning a dog spoiled several pieces that were laid after souring on the place where he was skinned.

Souring with sour milk or vegetable acid is at this time quite given up, though the writer speaks of cart loads of lemons, crab-apples, etc., which were formerly brought to the printing grounds; but oil of vitriol was alone used, about 2 gallons to 100 gallons of water, and the goods passed through it warm, "then washed, run between the squeezers, and as usual hang them on the stakes, or in the drying house, previous to being calendered."

The methods of washing cloth are said to have been very various and amusing to think of, "battledores, sticks, wash-wheels and the like, most of which tend considerably to injure the cloth (this, however, is a circumstance very likely not much desired to be prevented by printers); the dumb-planker or *wooden-man* now seems to have the preference." It is further said that the wash-wheel had formerly the preference, but it had had its day, if this be the same as the dash-wheel as seems probable, it lasted a good many years after this prediction, and is to be seen yet, but the "dumb-planker" or "wooden man" whatever such an apparatus might have been, is quite unknown to this generation even by name.

Calendering follows, and stress is laid upon the necessity of keeping the weft threads right, and the injury that comes, if by bad calendering, the threads lay obliquely on the table when printed, for in after processes they come straight and spoil the patterns.

There would seem to be two different treatments for cleansing cloth after printing and before dyeing; the first mentioned is to enter the goods into a copper of hot bran liquor, and "winch them as quickly as possible, otherwise the colour may start or run;" this operation was considered completed when the sightening was taken off, and due stress is laid upon the fact that some kinds of thickening, as paste

work, require more time and hotter fluids than others. The next mentioned is dunging : "the use of this operation is said to hinder the white part of the cloth, or that part whatever it may be which is to appear white, being stained by the superfluous colour, or according to the usual phrase of copper-men, it is to guard the colour and prevent marking off." It would seem probable that the use of cow-dung came after that of bran, and as an improvement ; this is the earliest account that we know of which describes the dunging operation and explains it well enough ; earlier than this cow-dung was used for clearing printed goods, but at that time it was certainly not used as described in this work.

The dyeing in madder either alone or with sumach is fairly well described, many goods were sumached separately before dyeing in madder, there is no mention of the use of soap in clearing or brightening madder work, the dyeing is followed by washing, and then passing in hot bran and water ; sometimes the whites are quite good after branning, if not, the goods are laid out upon the grass to be bleached by sun and air.

Colour-making occupies a large part of the work, but as before stated, there are no receipts for colours given, not, as the writer says, that it would "be disclosing secrets to say that to make black, take so much iron liquor, so much water, so much flour, boil them so long, &c. ; or so much alum, so much Sat. Sac., &c., for other colours ; for the secrets are in a rigid attention to those circumstances under which they may be applied, and all these cannot be specified in a recipe." In another place he states that there are very few good colour-mixers, and he declines to give receipts, as they "would not avail much, but on the contrary might do considerable injury by throwing out a stimulus to numbers who vaguely dip into the practice of colour-making, particularly in chemical processes, and hence too frequently dedicate their time and attention to what in the end brings disappointment and regret." Whether by design, as the author intimates, or from not being able to enter satisfactorily into the subject from want of knowledge, all this part of the book would

prove very disappointing to any one who might at the date of its publication desire to know how colours were made, or to any one now curious as to the exact processes followed; for it contains hardly anything which could not be found in the chemical books at that time in existence. There is sufficient evidence in the text to prove that O'Brien knew a good deal about the processes subsequent to printing, and something also of the conditions necessary to success with regard to several colours; but it must remain doubtful whether what he has written in this part of his book is deliberately intended to be wrapped in mystery and obscurity, or whether he meant to conceal his want of practical knowledge by a shew of chemical learning which has really very little bearing or application to the subject of the treatise. There are, however, some extracts which may be made to illustrate the treatment of the subject in the more practical paragraphs:

"The most durable Black and Purples are brought up in madder, by the agency of iron liquor; Reds by alum and occasionally tartar, salt of lead and iron liquor, to vary the hue to a Pink, a Blossom, a Chocolate, &c. Yellows in weld, by alum and tartar; Olives, Drabs, &c., by alum, tartar, and iron liquor; Doves, Browns, Greens, &c., in Sumach, Fustic, Greenwood, &c., by alum, tartar, and iron liquor; Blue from Indigo or woad, by the agency of ash, lime, and orpiment.

"Less permanent blacks, reds, purples, pearls, &c., are brought up in logwood, brazil, bark, &c., by the agency of iron liquor, galls, copperas, &c., but in skilful hands are to be much improved.

"Chemical browns, buffs, pale greens, blue, salmon, and other colours are, by the agency of Tar acid, Iron liquor, Verdigris, Woad, Annatto, &c., brought up or struck with lime, and other colours, such as berry yellow, pencilled blue, procured from indigo, &c., require streaming or rinsing in water only.

"For conveying these mixtures to the cloth, various articles are necessary to be used according to certain circumstances; these vehicles are gums and pastes; paste being of a more compact consistency than gum diluted, is used when lines or fine bodies or shades

are required to be accurately expressed ; diluted gum is more used in conveying solid bodies, in which no great accuracy of shape is required.

“Of gums, tragacanth has several advantages, and if properly managed would distribute as well as the arabic, but this article, as well as the oak-gall, is not always made the most of.

It is noted that “kermes was much used formerly by dyers, but cochineal is now substituted;” raisins in a mixture of indigo and alkali are said to throw up a copper coloured scum which gives a dye in a moment. Upon the relative goodness of colours produced at this time and formerly, there is a note as follows :

“It is here offered to set persons right in respect to colours, who affect to say that as good were done fifty or sixty years past, or as good were done two thousand years or more past, the very means as well as articles being of as ancient a standing, indeed the origin can hardly be traced; so in printing, the method immemorial has been by using alum, etc., to procure and fix the colouring particles, it may even be said what we call new colours have been produced many years past, under different appearances. If there be any real improvement, a principal one is in the mode of cleansing the cloth, and that perhaps is only in being rather more expeditiously performed than before.”

Referring to what were then called “chemical colours,” which were of a loose class similar to what are called “spirit colours” at present, the writer gives the reason for not entering into details that if it were known that these colours could be applied “with little trouble and small expence, numbers of indigent or desperate adventurers would naturally rush into the business ; and, by their mutual underworking and underselling efforts, calico-printing would soon lose its respectability; and (in the drapers’ phrase) prints in general become vulgar, and within the reach of those who have but little to spare, other articles must be substituted more worth the notice of persons of fashion or taste.” Of the writer’s intimate knowledge of various London printhouses there is abundant evidence, a good deal of gossiping is indulged in

which is sometimes amusing, he mentions Arbuthnots, who made some stir with green stalks on chintz, but the colour was very loose and soon "flew" leaving the flowers scattered here and there without stalks or any other appendage. Preston's chemical colours a few years afterwards made some noise, but a report was spread that they were oil colours and that the heat of a fire would destroy them, and they were soon extinguished; a blue and gold or black and orange style, said to be Naylor's invention, were also in loose colours, "from the ease and facility of its execution it drew many into the business that perhaps now wish they could eligibly quit it;" for the price of the work "had decreased from twelve pence or more per yard for printing down to three halfpence or even five farthings." We are told that "it is notorious that in many commissioned and other shops, the lowest chemical work, even with such colour as almost, literally speaking, would shake off, is warranted and ticketed as fast and often called chintz." The first intimation of the use of tin salts for red is given here, a great sum having been paid for the receipt by Nixons as the author believes, but details are wanting to know with certainty whether this was a madder red or not. Endeavours were made at this time to print upon mixed vegetable and animal fibres "but the difference of the substances not being provided for, the endeavour failed." "A bright or pale blue green from verdigris and spirit of sal ammoniac, and sometimes tartar; vinegar was formerly used till the ammoniac was introduced by a chemist at Manchester." A note is appended to the end of the section upon colour-making to the effect that "C. O'Brien will give any one, who is known to him, as of congenial wishes with himself, particular and useful intimation respecting them (chemical tests) by applying to him personally, or at his house, Islington, his views being (as several times said) to advance the respectability of the business beyond every other concern."

Reference is made to a case of close imitation of a pattern of Greaves, Newton, and Co., by Watson and Co., which came before Lord Kenyon, who expressed strong reprobation of the practice, and his determination to punish severely the parties

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to such piracy. The question of the country *versus* town printers is alluded to, and surprise expressed at the rapidity with which the country printers produced some copies of town prints, though done in a clumsy and inferior manner. It is stated that "the infatuation of setting up printing grounds in the country on a monopolizing or underselling plan, has like other furors had its paroxysm, and the fallacy of the prediction that the business would be nearly all done in the country is now evident enough."

It is admitted that many improvements have sprung from the country, and we come upon the earliest contemporary notice of printing from engraved cylinders, then in its earliest infancy, which occurs in the following passage:—

"Innovations, particularly on a mechanical principle, are spreading pretty widely in the country; and machines of various constructions are increasing about town; and perhaps many town printers will hardly credit that engraved cylinders perform as expeditiously as the common pin ones, that a machine for block printing was invented and used some time, with which anyone could print as easily as turn a winch (the specification for a patent was even made out) and that in machine printing, four cylinders may be used at once in different colours.

The writer can speak of this with confidence, having the advantage of knowing what has been done, and what has been further attempted; and was absolutely in a concern where an almost general course of printing by machines only was to have been attempted, a system being formed for that purpose; but certain considerations, among which the idea of such modes being ultimately injurious, from enabling the proprietors to underwork others, operating not a little with him, set the plan aside.

Shortly before the publication of this book, there occurred what is believed to be, the largest and most disastrous commercial failure in the print trade which has ever happened in England, it was that of the firm of Livsey, Hargreave, Anstie, Smith, and Hall, of Mosney, Walton-in-the-Dale, Lancashire. It was with this firm that Thomas Bell, the inventor of the printing machine was employed, and here was

brought out and partly developed, but a short time before the failure, the system of machine printing, which was to create so complete a revolution in the trade. The firm of Livsey and Co. was noted for its readiness to adopt all seeming improvements in the business of calico printing, but these could not preserve it from a tremendous crash. We think it worth while to reprint what O'Brien says about this house :

"It is said that this place was the means of giving bread to near 20,000 persons ; cloth in whitstering has occupied ground twelve miles in length, near 300 tables have been employed, and near 40 coppers at work at one time, 6 or 700 cylinders have been cut or pinned, common prints, etc. innumerable . . . but the price of labour was latterly reduced as much as possible, by converting, (as done at other places) herds of Lancashire boors into drawers, cutters, printers, machine workers, etc., and the work was proportionably execrable.

Of the failure it may be said, who in times past would have believed, or who in times to come will, that a connection reputedly worth above £150,000 at its commencement, should in a few years crumble under the deficiency of near a million and a half ; and that among those involved in the accommodation labyrinth, who fell in consequence (exclusive of Gibson and Johnson), some were for 10 or 20,000 pounds who comparatively speaking possessed little indeed ? saying nothing of those who lingered some time, or those who were more or less shaken, or may be shaking at this moment.

It must however, be observed that in trying to reinstate the firm, it was endeavoured to prove, that if it were supported till affairs could be arranged, there would be a balance in hand of 60,000 pounds, but the attempt was in vain ; the answer in general being that such egregious folly and extreme madness had little title to either succour for the present or confidence for the future.

As to the manœuvrings to raise supplies, they were carried to such enormous and unprecedented heighths, branched out into such complicated mazes and so finely spun as hitherto to have baffled the powers of a Thurlowe or a Kenyon to unravel."

The great rivals to the Livsey's, of Mosney, were the Peel's, of Bury, but while the one house sunk in failure, the other

increased in prosperity; the principal of the latter house seems to have excited the admiration of our author, for he says he turned out respectable work, and that he must be a superior man to have risen to what he is, and that unless vague politics distract his attention (he having gone into parliament), "he is a man of resolution and enterprise, whom other printers, a very few excepted, have either to fear or emulate." But the curiosity of our author led him to study a pamphlet of Peel's which was attracting attention, and it gives him a chance to say "most men of business in what they write have naturally an eye to their immediate vocations and interests, thus Mr. P——l dwells upon the increase of manufacture, but passes over those practices that, however they over-load the market, lessen the value of commodities, and is silent about that respectability which keeps up the spirit of any profession, or that is a proper inducement to genius to exert itself; for of the vast quantities he has himself thrown upon the market, a great part is well-known to have cost him little on the score of design and execution, the sale at the same time being undoubted." Again, speaking of what improvements might be made in printing by emulation, he exclaims, doubtless referring to the same person as in the last paragraph,

"What is it a certain senatorial Printer would not attempt were he in a line of commanding a price? for who is more capable or spirited? in short, what is it any man would not attempt, whose maxim is 'A man may be a Lord if he will!'"

Altogether this is a very remarkable book, evidently the production of a man of strong natural abilities, of great powers of observation, and of wide sympathies with every department of the business with which he was connected; the work is important and interesting as shewing the state of affairs in the London print field when it began to suffer severely from a competition with the Lancashire houses, a competition which was in a few years to be followed by an almost complete transfer of the business to the North. The disastrous failure of the Mosney printers gave some colour to

the idea expressed by our author that London would still continue the head quarters of printing, but greater natural advantages, greater energy, and a greater expansion of the cotton trade combined to make Lancashire, what it still remains, the most important centre of textile printing.

2. *The Printing Machine of Thomas Bell.*

THE mention of the introduction of the cylinder printing machine in the preceding article, and the references to the firm of Livsey and Co., where Bell's machine was first put into use, has induced us to believe that a reproduction of the drawing of this machine from the specification, and a description of it as given by Bell would be interesting to our readers. This patent is dated November 12th, 1783, and entitled "A new and peculiar art or method of printing with one colour, or with various colours at the same time, on linnens, lawns, or cambricks, cottons, calicoes and muslins, silks, silk and stuffs, and any other species or kind of linnen cloth or manufactured goods whatever." Thomas Bell is described as of Mosney, in the county of Lancaster, copper-plate printer, and the nature of the invention is declared as follows:—It consists in the using, for the purpose of printing as aforesaid, the machine or piece of machinery particularly described in the plan hereunto annexed, or hereunder drawn, and which machine or piece of machinery consists of the several parts, and is to be constructed, put together, and used in the manner described in the said plan, and the explanation subjoined thereto, and which machine or piece of machinery, and the rollers therein contained may be made of wood, copper, iron, pewter, or any other kind of metal or material whatsoever that rollers are or can be made of. Different patterns may also be added to the rollers, which can be put on and off at pleasure."

The description of the drawing so far as relates to the parts we have caused to be reproduced runs as follows:—

Fig. 1 (the upper figure) represents an end view of the machine, with all the wheels necessary for the printing of six colours.

A the end of the frame or head for supporting the main roll and printing rollers.

B is an iron hoop put round the head A.

C is the ground sill into which the foot of the head is morticed.

D a centre for a handle to turn the nut E, which strikes into the great wheel F, and which gives motion to the wheels G, which are fixed on the centres of the printing rollers *h*.

G is an iron carriage for the nut E and great wheel F, which carriage is fastened to the head A by screws or otherwise.

i the heads of the forks that support the printing rollers *h*, the lower ends of which go through the iron hoop B, and are fastened there by cotterils, screws, or otherwise.

H the ends of the boxes which contain the colour, to one side of which the steel doctors are fixed which clean the printing rollers.

k are iron screws fixed into the iron hoop B for carrying the colour boxes and steel springs as in the other figure.

l is a foot made of iron for bringing back the main roll to make the joinings.

The lower figure represents the other end of the machine.

A the end of the frame or head for supporting the main roll and printing rollers.

B the iron hoop as in fig. 1.

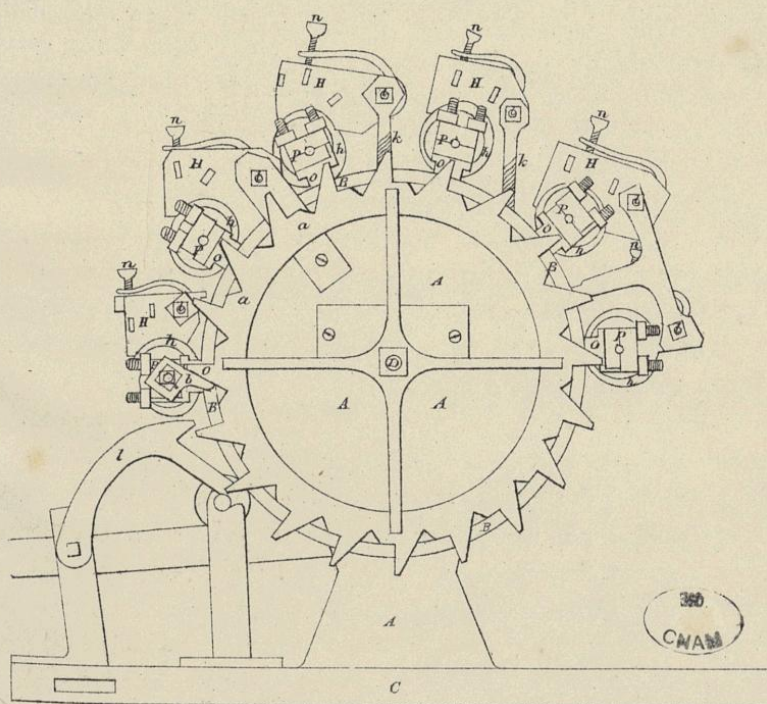
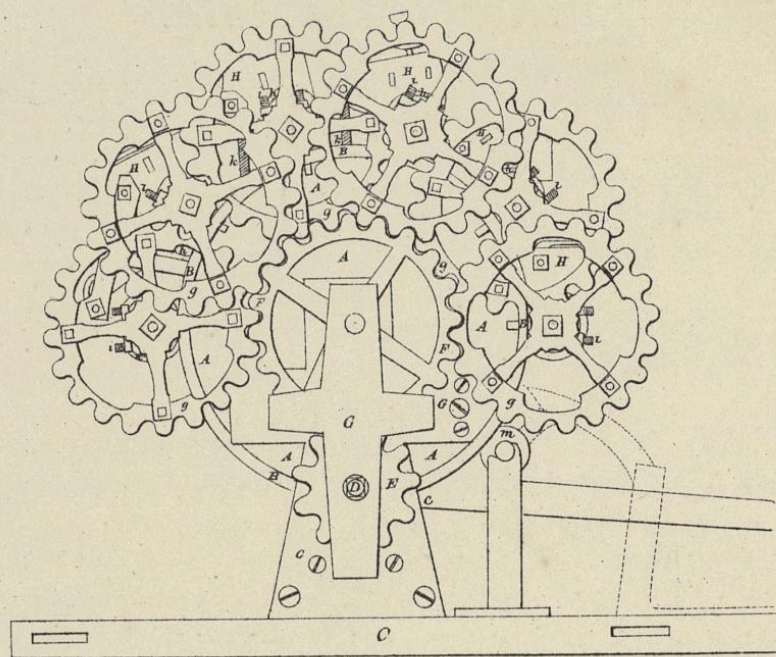
C the ground sill as in fig. 1.

D the centre of the main roll upon which is fixed the pitch wheel *a*.

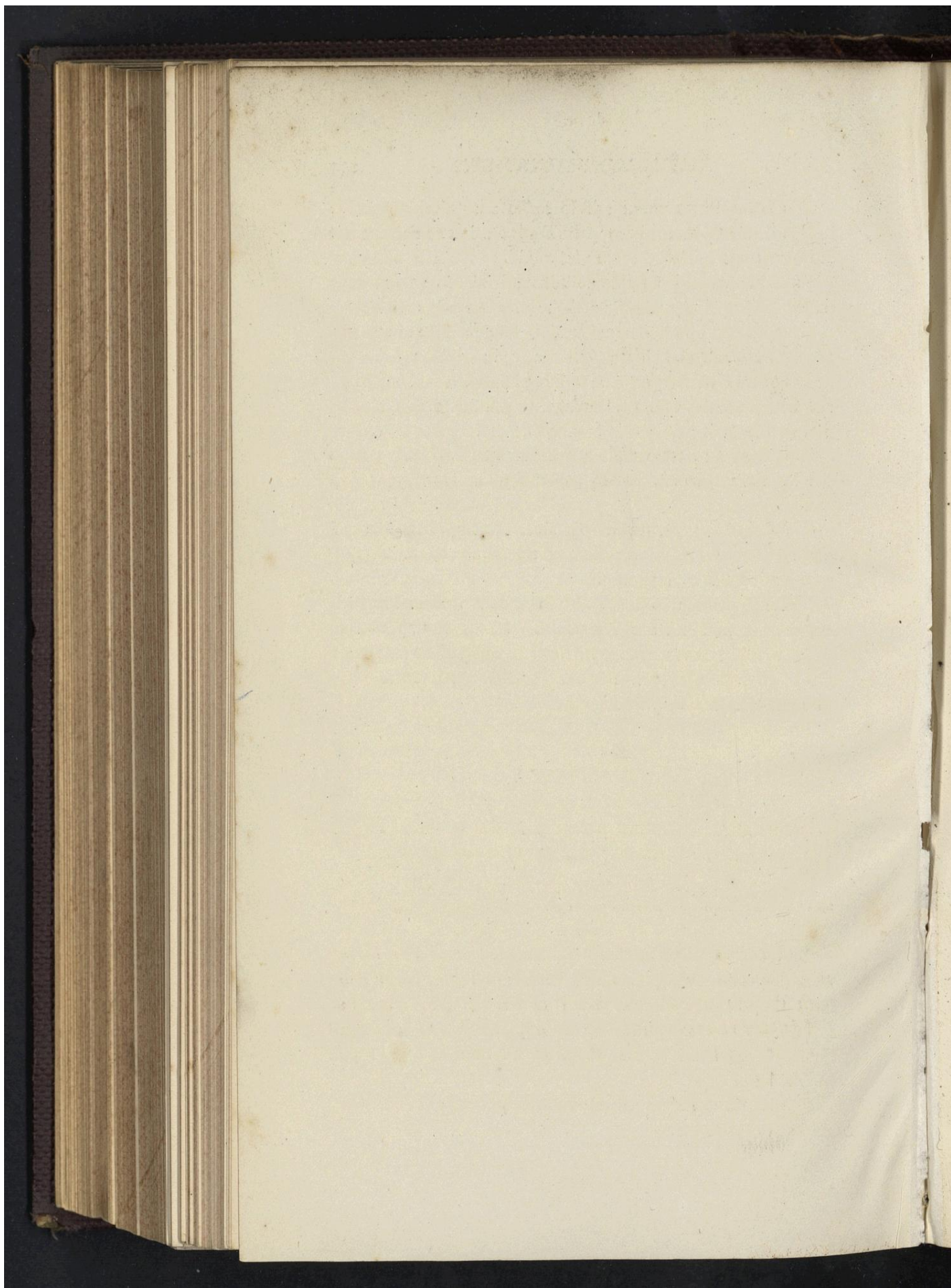
b is a catch fixed upon the centre of the first printing roll *h*, and strikes into the pitch wheel *a* once in every revolution of the printing roll *h*, which brings the main roll in contact with the printing roll and adjusts the joinings.

l is the iron foot as in fig. 1, which being acted upon by the catch *b*, falls into the pitch wheel *a*, and brings back the main roll to make the joinings.

h the ends of the printing rollers.



Six-colour Printing Machine.—Bell's Patent, 1783.



H the ends of the boxes which contain the colour.

k iron screws fastened into the iron hoop B, which supports the colour boxes H.

l are the ends of the iron bars which go across the frame on which the colour boxes H and steel springs *m* are fixed.

n are screws which go through the ends of the springs and press upon the top of the doctor.

O the forks or carriages for printing rollers.

P are brass steps betwixt which the centres of the printing rollers run.

The cloth is represented by the two lines on the right of the top figure, entering by the small roller *m*, and coming out at *c*.

There are other figures in the large drawing appended to the specification, shewing details of the colour boxes, doctors, and cloth feeding apparatus.

There is another patent to Thomas Bell, the elder (of the same place and business, but whether the word "elder" indicates another person or not we have no means of knowing), dated August 4th, 1784, but the drawing attached is quite different, and not very intelligible.

3. *Critical and Historical Notes concerning the Production of Adrianople or Turkey Red, and the Theory of this Colour.**

BY THEODORE CHATEAU.

Corresponding Member of the Industrial Societies of Mulhouse and Amiens, etc., etc.

THIS fourth and last part will be occupied with an account, chronologically arranged, of the various opinions which have been put forward upon the theory of the Turkey red process.

The earliest speculations we are acquainted with are those given by Macquer in his Chemical Dictionary, 1778; this author says:

*Abstracted and condensed from the "Moniteur Scientifique," vi. (3), p. 786.
Continued from Vol. ii., p. 33, Textile Colourist.

In considering the effect of the many complicated operations which constitute the Turkey red process by which cotton is dyed a madder red infinitely more beautiful and agreeable than can be obtained by the common methods, I have been struck with the singularity of the system of aluming, which consists in mixing a considerable portion of fixed alkali with the solution of alum before it is applied to the cotton. As the alum most certainly suffers decomposition by the alkali in this treatment, I was desirous to discover what was the action. I found that while fixed alkali precipitates the earth of the alum, it can at the same time dissolve a considerable quantity, and form an alkaline salt of the earthy base of the alum, which becomes a true mordant in this kind of dyeing. I ascertained by satisfactory experiment,

(1) That the fixed and volatile alkalis, especially when caustic, are able to dissolve and bring into the saline state a considerable quantity of the earth of alum, even in the moist way, and that by calcination the fixed alkalis could dissolve a slightly greater quantity of this earth.

(2) That the alkaline earthy salt was decomposed by water alone, and still more effectually by a decoction of madder or other dyestuffs, that the earth (alumina) seized the colour and formed a lake with it, or a coloured precipitate, as do the mordants which are composed of an acid, and an earth or a metal.

(3) I found by a number of experiments that cotton which was impregnated with a strong solution of this alkaline mordant, without any other preliminary preparation beyond cleansing and galling, attracted in the madder dye a red colour much more full and more beautiful than could be obtained by means of alum; and consequently it is to this alkaline aluming that Turkey red chiefly owes its superiority, the other preparations of the cotton in this process may contribute to the beauty and the fastness of this colour, but only in so much as they dispose it to receive and retain a greater quantity of the alkaline mordant with the alumina base, which is actually the soul of the colour.

In the *Journal de St. Petersbourg* for the year 1776, which gives the account of the travels of Pallas, who described the Turkey red process he had seen followed in the East; there is a note by the editor, which has considerable interest in an historical point of view, as concerning the theories of Turkey red. The note is as follows :—The gelatine, glue, or ox blood, with the base of the alum, form the proper mordant for fixing the colouring matter of madder upon cotton ; but this triple combination owes its permanence in part to the galling, that is to say, to the tanning principle of the fustic or gall nuts, which makes the gelatine applied to the cotton become insoluble. The weak alkaline treatments serve to re-dissolve the fatty matters not combined, the boilings with saponaceous and oily mixtures soften the thread, and this series of operations several times repeated give to the Turkey red when soaped a degree of fastness nearly perfect.*

Pileur d'Alpigny, in his treatise upon dyeing (1776 and 1798), gives the following as his ideas of the theory of Turkey red :—In dyeing the cotton, sheep's dung is mixed with a ley of fixed alkali which retains the volatile principles of the excrements and consequently prevents putrefaction. When the cotton is several times worked in this soapy liquid it is impregnated with the alkaline principles which predominate ; and it is known by experience that substances which have been once impregnated with volatile alkali, as for example the chemical utensils used to extract it, retain a strong odour for a long time which resembles musk, and which is difficult to remove even by cleaning with sand, ashes, or soap. Each time that the cotton is dried out of this liquor, the evaporation of the water causes the alkaline principles, which change into earth, to have a stronger adhesion to the pores of the cotton ; there results, from the union of this earth with a portion of the oil which has been used, a cement which is afterwards

* M. Chateau remarks upon this note that the scientific expressions used in it are of so modern a form that they by no means correspond to the scientific style used at the date of 1776, which is properly represented by the language of Macquer and Pileur d'Alpigny. Therefore he gives the date with this explanation, not having himself seen the *Journal de St. Petersbourg* ; he does not, however, say where he found this note himself.

perfected by the alum ; and this is in a few words the theory of the fastness of this dye.

Chaptal gives as follows :—The operations commence by cleansing the cotton or opening its pores so that it may more readily accept the mordants.

Afterwards it is saturated with oil which is properly diluted by means of weak alkaline leys ; the cotton is several times steeped so as to better spread the oil and distribute it more equally in all parts. After that the cloth is galled, and here the oil forms a first combination with the gall nuts, as may be seen by mixing a solution of soap with a decoction of galls.

This first combination of oil with galls possesses a great affinity for the colouring matter of madder, but the colour is very dark, heavy, and difficult to brighten. To remedy this it is necessary to add to this first combination a third body which will render the compound more fit to fix the colour and give it brightness, this third principle is the alumina of the alum.

To appreciate the action of alum in dyeing it is sufficient to mix a decoction of gall nuts with a solution of alum, the mixture at once becomes opaque and there is a grey precipitate formed which when dried is insoluble in water and nearly so in alkalis.

Here then is a combination of three principles fixed to the cotton by strong affinity and having a strong attraction for the colouring matter of madder. When this triple mordant is saturated with all the colouring matter which it is able to take, the washings in water and the brightenings by boiling in alkaline leys can only deprive the cotton of that portion of the colouring matter which is not fixed by the mordant and which adheres either to the cotton itself or to some mordant not itself fixed. After these operations the cotton retains only oil, galls, and alum, strongly combined and saturated with the colouring principle. Analysis can demonstrate the existence of all these bodies.

The acid composition used for the dyed colour acts only upon the colouring matter itself, which it brightens.

Bancroft adopted the conclusions of *Chaptal* and en-

deavoured to obtain the triple combination by simpler means than those in practical use; but the experiments were not successful and he never obtained a red colour comparable in beauty and fastness to that produced in the regular manner. He had an idea that the fastness of madder colours depended in a great measure upon some unknown principle existing either in the blood or excrements used.

Vutich was of opinion that the cotton was opened by the oils and then it took the mordant and colouring matter more readily, not that the soap or oil entered into any combination with the cotton. By the treatment with alkalies the oil which was contained in the cotton became saponified and washed away, so that the cotton did not increase in weight. By galling and aluming the cotton experienced a sort of tanning by means of which the saline parts of the blood and the colouring matter of the madder was fixed. In the dye bath the free acids of the madder combined with the albumen of the blood to form a soapy combination, and the phosphate of iron formed with the gallic acid of the cotton a black precipitate; the colouring matter of the madder became free and combined with the cotton. By boiling the dyed cotton in alkaline liquids the compounds of acid and albumen just mentioned and the phosphate of iron retained by the cotton were dissolved. Quoted by Leuchs, i., p. 304.

Dingler says the cotton is penetrated by the oil in the treatment by the emulsions, this oil becomes changed by repeated dryings and exposure to the air, it absorbs oxygen, and in this changed state combines in an intimate manner with the fibres of cotton, which become increased in weight during the operation. The excrementious matters, as well as fermentation, accelerate the oxidation, and for this reason impure oil is preferred, to pure oil.

The treatments which follow with alkaline liquids are for the purpose of removing the oil which has not become oxygenated, and a strong drying afterwards should completely change that which still remains adhering to the fibres; the aluming which follows produces a combination of the alum with the cotton; the galling tans the fibres which have com-

bined with the oxidized oil and produce a compound of changed oil, alum, and tannin, which cause the colour to be so fast. The aim of the remaining operations is self evident.

Vitalis expresses himself as follows:—Although far from thinking that the cleansing operations have the effect of dilating the pores of the material to be dyed or of clearing them from obstructive matters, still we think it undeniable that the intention of these operations is to remove from the fibres a greasy or resinous matter which envelopes them and fills up the interstices diffused amongst the filaments.

It is this greasy or resinous matter which hides the white colour of the fibre, and makes it have a less affinity for water and the colouring matters which it has to receive. It is for this reason, that as a rule when it is wished to have the brightest colours and give them the highest possible degree of brilliancy and fire, that it is indispensable to push on the cleansing, and even the bleaching as far as possible without actually injuring the fibre, for these operations always lead to a loss of weight and substance, which is more or less considerable, and which cannot be avoided.

It is true that it is not necessary to bleach cotton before dyeing it Turkey red; but in the case of flax or linen it is always better to purge these fibres as much as possible from the resinous substance which colours their surface, and it is very likely that a soda treatment is sufficient for cotton because it is less contaminated with this substance.

The treatment with excrement of sheep can have no other aim than to assimilate cotton or linen, which are vegetable substances, to the nature of animal fibres, or, as it is commonly said, to *animalise* them to a certain degree by combining them with the fatty matter, which is a constituent of the excrement of ruminant quadrupeds as the sheep. This animal matter, dissolved in the alkaline soda ley, is divided in the finest possible state, and consequently is in the most favourable condition to enter into combination with the cotton. This the author believes he has demonstrated in a memoir presented to the Institute of France in 1806, and printed in the *Journal de Physique*.

In this particular, art has imitated nature with some success.

The white baths which follow the dung baths carry to the cotton the mucilaginous matters mixed with oil, and which, as we have seen, concur with the nitrogenized matters furnished by the sheep's dung to precipitate easily the colouring matter of the madder upon the cotton. The property which the fatty principle enjoys of combining with the colouring matter leads to the belief that this substance itself has a useful action.

It is easy to understand from this why the cotton should be disposed to receive the colouring matter of madder, when it has been well prepared by a certain number of treatments of a weak nature, but frequently repeated, so as to contrive that the fibre should gradually be impregnated with this kind of mordant, and at length completely charged with it to the extent of its capacity, when it is saturated so as to obtain solid and full colours.

With all the care which may be taken in pressing, wringing, or squeezing the cotton out of the dung and oil baths, it is impossible not to leave a certain quantity of the liquids adhering merely to the surface of the cotton which have not really combined with it in a perfect manner, and it is easy to conceive that these superfluous liquids would seriously interfere with the effects of the following applications if care was not taken to remove them by the operations of steeping in alkalies and washing.

As to the drying which follows most of the operations, its necessity becomes evident upon considering that the humidity of the cloth is an obstruction to the combination of a succeeding mordant. And for this reason it is not always sufficient to dry at the temperature of the air but to complete it in a stove heated considerably, especially in winter and damp weather.

It will be impossible to give an accurate explanation of the effects of the galling operations until it is known what are the real principles contained in gall nuts. It appears certain that they contain a peculiar acid called gallic acid, but what is the tannin which always accompanies this acid? The properties of this tannin are no better known now than in the time of

Berthollet who regarded it as an astringent principle which however no one has succeeded in isolating. It is, however, certain that gall nuts not only perform the office of a mordant, but of a mordant of the most powerful nature, acting either directly upon the oiled cotton or perhaps upon the mordant of the alum.

Alum plays a most important part in the Turkey red dyeing, but what is this part? This question can only be answered when we perfectly understand what takes place when this substance is brought into contact with a solution of gall nuts. It is well known that gall nuts produce a precipitate in a solution of alum, which Mr. Henry states is nothing else but alumina separated from its sulphuric acid. It may then be supposed that when the galled cotton is passed into a solution of alum this salt is decomposed in such a manner that the alumina leaves the acid which held it in solution in order to combine with the principles, whatever they may be, derived from the galls and which have been fixed upon the cotton in the galling process.

A first lesson to be drawn from this is that to effect this precipitation of the alumina and combine it with the products of the gall nuts the aluming must be performed at a moderate degree of heat, about 80° F., for at a higher temperature the alumina would precipitate too quickly and in too great a quantity so as not to have time to combine with the gall nuts, and thus a great portion would not enter into combination; and, secondly, it is not less evident that the combination of the alumina with the galls forms a new compound mordant, which unites with the mordants which the oily and excrementious matters have already supplied.

It may be remarked that it is not without reason that in the aluming the precaution is taken of adding a certain portion of alkali to the alum, about 1 oz. of soda to 1 lb. of alum. For alum is an acid salt and the excess of acid being saturated by the soda is prevented from having any injurious action upon the cotton. Another advantage which results from this is that the affinity of the alumina for the galls augments in proportion as it is less restrained by the affinity

which it has for the sulphuric acid, from which it follows that the new combination should be effected with greater facility. It might be possible to dispense with saturating the alum in cases where the cotton had previously been treated with a great number of salts in a strong degree, as was formerly practised.

It is probable also that the oil baths which the cotton has received previously to the passage in alum may contribute in some degree to the decomposition with the formation of a species of aluminous soap, which, fixing upon the cotton, would form a very fast mordant, as it is completely insoluble in water.

Vitalis then gives the theory of Macquer, which may be found at the commencement of this part of the memoir. He adds: Notwithstanding the respect which we have for the authority of Macquer, we cannot wholly agree in his opinion.

We admit, with this illustrious chemist, that the saturation of the alum by an alkali, or rather the addition of an alkali to the alum, produces good effects in the mordanting as we have stated above, but this modification in the employ of the alum does not appear to us, as Macquer seems to think, the principal cause of the superiority of the colour of the Turkey red.

In fact, the quantity of soda which is added to the alum, supposing it to amount to an eighth part of the weight of the salt, hardly suffices to saturate the excess of the sulphuric acid which is found in the alum. The alum cannot therefore become an alkaline mordant capable of dissolving a great quantity of alumina, especially as the alkali used is far from being in the caustic state, as it ought to be according to Macquer, in order that it should dissolve and place in a saline condition a sufficiently large amount of the earth of alum, but is on the contrary combined with a notable quantity of carbonic acid, or according to the language of the older chemists, it is in the state of aerated alkali.

In confirmation of this reasoning there is a decisive fact; it is that by treating cotton, prepared by galling, with alum prepared by Macquer's method it is impossible to obtain by dyeing a colour so bright or so fast as that produced by the

ordinary treatments with oil baths, and we may say that we believe it is chiefly to this preparation that the Turkey red owes its superiority over the madder red obtained on cotton which has not been subjected to this treatment.

Cotton prepared by the Turkey red process seizes with avidity upon the colouring matter in the process of dyeing, the colour fixes firmly upon the cotton by the assistance of the mordants which it has received and with which it has been previously combined ; these are, the fatty matter of the sheep dung, the oily principles, the mordant of galls and alum, to which must be added the albumen furnished by the blood used in the dyeing and perhaps other animal principles and salts contained in this substance, for it is proved that the colouring matter of the blood takes no part in the dyeing and does not increase the colour from the madder.

Cotton only acquires a dull and dark coloured red bordering on brown in the actual dyeing which has nothing agreeable about it ; it was necessary therefore to contrive some means of removing this dull colour and produce a clear definite colour. For this purpose the brightening operations are undertaken, the effect of which is to make the red appear by removing and dissolving a brown matter which masked it. The red thus obtained is pleasing, and for a long time no better was desired, especially after it had become somewhat brighter by a few days' exposure on grass. But by an additional operation called *rosage* the colour acquires a brilliancy and lustre much superior to that resulting from the old treatment alone. To obtain this effect the cotton is boiled during four or five hours with a solution of white soap to which has been added a solution of salt of tin previously treated with nitric acid. It appears that in this operation the soap and the salt of tin are mutually decomposed, the acid of the tin salt taking the soda and the separated oil uniting with the oxide of tin to form an acid metallic soap, which gives that clearness and brilliancy to the red so agreeable to the eye.

Gonfreville, who described the Indian process of red dyeing in which no alum is used, endeavoured to explain how it was that the result was still a very fast colour, and believed he

found the explanation in the fact that the ashes used for alkali contained some alumina, and that this earth was in alkaline solution; but very little could possibly be dissolved and hence the necessity the dyers were under of giving the cotton ten to twelve successive baths of these ashes. The cloths being previously oiled, Gonfreville thinks that there was formation of something like oleate of alumina on the fibre which was the actual mordant.

[*To be continued.*]

4. *Note upon the Probable Constitution of Aniline Black.**

BY M. CH. GROSS RENAUD.

IN M. Antony Guyard's paper in the Bulletin of the Paris Chemical Society, vol. xxxv., p. 58, he draws the conclusion, without, however, giving any proofs, that aniline black is formed by the dehydration of emeraldine. The publication of this paper induces me to communicate some observations which I have made, and which led me to a similar conclusion.

It may be recollected that M. Rosenstiehl has recently shewn that the green or black from aniline, which can be obtained on cloth in a practical manner by means of chlorine compounds, is due to precisely the same oxygenated compounds of chlorine which give rise to aniline purple or violet. Hypochloric acid, acting upon a dilute solution of an aniline salt, gives the violet colour; acting upon calico impregnated with aniline salt, the vapours of the same acid give a green colour which, when the acid is washed away, becomes a blue-black, characterised by all the properties of aniline black.

If calico, impregnated with nitrate of aniline, be touched with sulphuric acid at 50° Tw., and some hypochlorite placed on the spot, a violet coloration is seen immediately. A

* Bull. de la Soc. Ind. de Rouen, iv., p. 183.

portion of the same calico in the dry state exposed to the vapours of hypochloric acid takes on the other hand a green colour, which turns to black in alkali.

Again, if a porcelain dish, covered on the interior with solution of nitrate of aniline, be exposed to the vapours of hypochloric acid, the first effect is to produce a violet colour, which passes into green as the coating of aniline salt becomes dry; if the dish be withdrawn from the acid vapours at the right stage the change from violet to green can be observed by simply drying in the air.

If hydrochloric acid be gradually added to a concentrated solution of aniline salt and chlorate of potash, it first produces a violet colour, which slowly passes to green and then to black; but if the solution be diluted the hydrochloric acid produces only a violet colour, and the action goes no further.

The following experiments can be easily made:—Prepare a solution containing

2500 grains hot water,
200 grains crystallized nitrate of aniline,
90 grains chlorate of potash,

and first add 30 grains measure of strong sulphuric acid to 100 grains of the solution; by carefully stirring a dark violet colour will be obtained in a few moments, which, if thrown into a large quantity of water deposits only an inconsiderable amount of black matter upon standing.

Secondly, leave the mixture alone, and in ten or fifteen minutes it becomes solid. The transformation is nearly complete in twenty minutes, and the whole being now thrown into water gives an abundant precipitate of aniline black, while the solution is nearly colourless.

If the above solution contains double the quantity of aniline salt the reaction is more active, and the aniline black is formed nearly instantaneously. If, on the contrary, it be very much diluted, the sulphuric acid will give the violet, if added in sufficient quantity, without any trace of black.

If a piece of calico be impregnated with a cold saturated solution of nitrate of aniline and divided into two parts, one of

which is dried, and both then suspended, the one dry and the other moist, in a receiver over aqueous solution of hypochloric acid, the moist piece will be coloured violet and the dry piece coloured dark green. As the humid piece becomes dry the violet becomes grey, and finally green.

M. Goppelsroeder, in his remarks upon electrolytic aniline black, says: "When a galvanic current, weak or strong, is passed through an aqueous solution cold or hot, dilute or concentrated, neutral or acid, of the hydrochlorate, sulphate or nitrate of aniline, it forms sooner or later at the positive pole, a green deposit which passes through violet, blue-violet, to dark indigo-blue."

What conclusion can be drawn from these various experiments? I am forcibly impressed with the idea that water has a considerable influence upon the formation of the aniline violet and black. In dilute solutions, or on wet cloth, it is always the violet which is produced; in strong solutions and on dry cloth, or in dry air, black is obtained. Whatever be the composition of the black colour for aniline, whether it contain salts of copper or vanadium, no black is obtained if there is an insufficient quantity of chlorate or aniline present.

The formation of these colours under the different circumstances would be easily explained if we could consider aniline black as dehydrated aniline violet. The idea of the dehydration of a substance when it is surrounded with moisture is somewhat repugnant to the intelligence; but examples of it are not rare. Stannous oxide precipitates as a white hydrate in dilute solutions, but as a black anhydrate in strong solutions; the dehydration of oxide of copper by boiling, and of ferric oxide under the same conditions, the crystallization of sulphate of soda in water in both the hydrated and anhydrous state, and other analogous and well-known phenomena, might be cited.

It is also known that if the quantity of salammoniac in aniline black colour be considerably increased, emeraldine is formed directly upon the cloth; it seems probable that the presence of a large amount of salammoniac hinders the com-

plete dehydration of the aniline violet, and this supposition receives support from the fact that the emeraldine is gradually transformed into aniline black.

In practical printing, the conditions necessary for the production of aniline black are not generally so strictly and accurately fulfilled that there may not be formed at the same time a certain proportion of mauveine and emeraldine; the blacks are therefore mixtures, and that is, no doubt, the cause why some authors have been led to suppose that there are several aniline blacks, but I am convinced that there is only one real aniline black properly so-called, by whatever means it has been formed.

In conclusion, I think that the experiments above detailed shew that it is possible

(1) That the action of oxygenated compounds of chlorine upon aniline, in presence of water or humidity, give birth to mauveine or violet.

(2) That the green or black colour is only produced in comparatively dry conditions.

(3) That emeraldine and aniline black appear to be derived from mauveine by a more or less perfect dehydration.

5. *Are Aniline Colours Poisonous?*

SINCE articles of apparel dyed with aniline colours came into extensive use there have been several cases in which the wearers have been said to suffer from local poisoning, sometimes in the feet from socks or stockings dyed various colours, other times in the head from hat linings, and various parts of the body from aniline-dyed garments worn in immediate contact with the skin. In some places restrictions have been placed by the governments or police upon the use of these colours both for dyeing and for colouring articles of food. The generally-known fact that fuchsine or magenta, the

principal colouring matter obtained from aniline, was made by means of a most poisonous substance—arsenic acid,—and that many or it may be said most samples of it yielded traces of arsenic when tested, gave probability to the popular supposition that it was an arsenical compound and consequently dangerous to health or life. It is, of course, well known that though magenta is made by means of arsenic, this metal is not a constituent part of the finished product, which in fact is not an arsenical compound, and that if arsenic be found in any samples of it offered for sale it is owing to want of skill or want of care in its manufacture. Magenta can be produced in other ways than by arsenic acid, and actually large quantities are made without ever coming into contact with arsenic in any form whatever. The question of whether pure magenta is a poisonous matter or not has recently been investigated by Professors Bergeron and Clouet, and we abstract what follows from a paper communicated by them to the Industrial Society of Rouen, 7th April, 1876.*

The Parisian police arrangements by implication permit, though they do not authorize, the use of aniline dyes for colouring articles of food. The actual colouring substances authorized by the regulations of the Parisian police to be used are—For blues—indigo and its compounds, and Prussian blue; for red—cochineal, carmine, carmine lake, Brazil wood lake, and archil; for yellow—saffron, Avignon and Persian berries, quercitron, fustic, aluminous lakes of yellow woods, and turmeric; for green—mixtures of the above yellows with Prussian blue; for violet, Prussian blue and carmine. The use of the following colouring matters is absolutely forbidden for articles of food:—Copper compounds, red lead, vermilion, chrome yellow, gamboge, arsenical greens, white lead and its derivatives. For colouring liqueurs, besides the above, logwood and ultramarine are permitted. No mention at all is made of the aniline colours.

The experiments of Professors Bergeron and Clouet are confined to the one colour of aniline, fuchsine, or magenta, and were made upon the pure colouring matter, that is, free from

* Bulletin of this Society, iv., p. 138.

arsenic or other metals ; in other words, upon a pure salt of rosaniline. The most opposite opinions have been expressed as to the physiological properties of magenta. Some have considered it as a most dangerous article ; others look upon it as inoffensive ; and others still have been led to believe that it was endowed with therapeutic powers which could be utilised in the treatment of certain diseases (chorea, &c.)

Amongst those who have considered magenta to be poisonous, Bergmann and Husemann, are cited, the latter of whom* seems to attribute an excessive activity to these colours, since he published a statement that several children had died from the effects of eating bonbons coloured by magenta. The colour in question was impure, containing arsenic, the quantity of which swallowed was estimated at about $\frac{1}{1000}$ part of a grain (from $\frac{1}{11}$ to $\frac{1}{18}$ of a milligramme). Notwithstanding this infinitesimal amount, the author attributed the deaths to the arsenic, because he thinks that arsenic forms very dangerous combinations with these colouring matters, on account of the intimate attraction they have for animal membranes.

Such a theory, the writers think, has no foundation in fact, and hardly deserves notice.

The majority of medical writers agree that magenta itself is certainly not actually poisonous, but that it may, of course, if impure from arsenic or other metals, be poisonous ; but Dr. Sonnenkalb states that if 1 per cent. of arsenic was present in magenta, its colouring power is so great that the quantity required to colour liqueurs, confectionery, jellies or ices would not have any poisonous effect.

In 1863 Dr. Charuet, in noticing an epidemic which occurred among the workmen in a magenta factory, said it could not be attributed to either nitro-benzine, aniline, or fuchsine (magenta), but was more probably due to the arsenic employed, for all the symptoms agreed with those of chronic arsenical poisoning. As to the use of aniline derivatives in medicine, it can only be said that they have been administered without producing any accidents or injurious effects.

* American Journal of Pharmacy, 1875, p. 210 ; and Repertoire de Pharmacie, 1875, p. 467. Vol. iii. New series.

In order to settle the question, the authors made a series of experiments upon men and animals, of which they give the details.

In the first experiment 5 centigrammes (about $\frac{3}{4}$ grain) of pure fuchsine dissolved in water was injected. The effects observable were that in two hours the urine was slightly tinged, the pulsations were slower after the absorption had taken place, the temperature fell slightly; the most remarkable thing being the disappearance of albumen from the urine of the subject, who had been long suffering from heart disease with albumenaria. A second experiment, with four times the quantity of magenta, gave similar results, the magenta taking about nine hours to be completely eliminated by the urine, which all the time was free from albumen; the subject felt a better appetite than ordinary.

In a third experiment 35 centigrammes (about 5 grains) of magenta was dissolved in sugar and water and swallowed. A bitter, astringent taste lasted for two hours, resembling at the end that of sulphate of copper. No particular action. In this and other experiments it is curious that the urine passed soon after taking the magenta is colourless, having lost its normal colour, and then becomes coloured with the magenta. A fourth experiment, in which 6 decigrammes of magenta were swallowed (about 9 grains) presented no striking phenomena; in a fifth experiment the dose was increased to one gramme (15.3 grains), there was a slight feeling of sickness and headache, but nothing more. Other experiments only confirmed those already given; only a small portion of the magenta is eliminated by the kidneys, the greater portion going off by the intestines.

These experiments, which were made upon the writers themselves, and repeated upon another person, prove that 15 grains of magenta could be taken daily without injury, and about 50 grains taken in eight consecutive days without perceptible effect. The quantity of magenta used in colouring wine may be taken as about one-tenth of a grain per quart, an amount absolutely insignificant as far as concerns health.

Experiments with larger quantities of magenta were made upon dogs, as much as 20 grammes (more than 300 grains) administered at one time did not produce any serious illness. It is, however, evident from the detailed symptoms, that the administration of such doses repeatedly have an injurious action, producing vomiting and other disturbances, from which the animal does not immediately recover.

The conclusion is that pure magenta is not at all poisonous, but the real danger is that impure magenta may be employed by ignorant or careless persons for colouring articles of food, and it is admitted that in this way serious accidents might occur.

6. *Experiments upon the uses of Aniline Black, by Vanadium, in Dyeing Woollen and Mixed Tissues.**

BY M. HOMMEY.

THE use of vanadium salts as applied to cotton goods having been studied and reported upon by several members of the Industrial Society, we undertook a series of experiments upon woollen and mixed goods, which having led to tolerably satisfactory results, we proceed to give an account of them.

The use of vanadium compounds has enabled us to obtain a fine black upon wool with comparative ease, a result which has hitherto been found impossible.

The methods which were previously known to us gave very bad blacks, either injuring the texture, or being too long and too difficult in their application to be practically applied; but with vanadium salts the difficulties are greatly decreased.

As M. Guyard has indicated, it is sufficient to steep the cloth in a bath of muriate of aniline, chlorate of potash, and a salt of vanadium, to permit the oxidation to proceed and to complete the development and oxidation of the black by a passage in a chromate bath.

There is no necessity for a previous preparation of the cloth. We have tried cloth prepared with bichromate and

* Bull. de la Soc. Ind. de Rouen, iv., p. 263.

with sulphate of copper and acid, according to the process of M. J. Persoz, but so far we have not seen any advantages which renders these additional operations advisable.

The steeping in the aniline bath should not be of long duration; we have obtained good results by leaving the cloth twenty or thirty minutes in the aniline bath, squeezing out, and placing it in a warm room; the day following the green was dark enough to allow the passage in bichromate to complete the raising of the black.

The proportions given by M. Guyard yield a black, but for wool we have found it advantageous to add as much as 1 per cent. of hydrochloric acid (10 grammes of acid per litre).

This addition depends upon the substances employed, and we have to provide for the neutralization or expulsion of the alkalis which have been used in cleansing the wool.

The proportions of materials are as follows:—

Water	10 gallons.
Muriate of aniline	8 lb.
Chlorate of potash	4 lb.
Hydrochloric acid	$\frac{1}{2}$ lb.
Vanadate of ammonia.....	70 grains.

These proportions gave us a dark black, which was fast enough to sustain washing and a good cleansing, and other operations to clear and brighten it. The cost price however seems to us too high.

[Here in the text is inserted a sample of thick and good cloth, the colour of which appears quite satisfactory.]

To obtain this black sound and even we found it advisable to impregnate the tissue with the solution of muriate of aniline and chlorate of potash, then to pass it between rollers to make it penetrate the interior of the cloth, and afterwards to repeat the operation with a bath containing the vanadium salts.

The application of this black may turn out of great service in stuffs which contain mixtures of wool and other fibrous matters as cotton.

Among the specimens shewn there are cloths with woollen warp and cotton weft, and another made with shoddy con-

taining cotton; we have also tried the colour on a mixed woollen and silk tissue, and the results in all cases are good.

By using this method there is no necessity for either dyeing or mordanting the vegetable fibres before dyeing the wool, nor of destroying the vegetable fibres by means of chemical agents, neither of any special method for dyeing up the cotton after the wool has been dyed.

Aniline black is developed more easily upon cotton than upon wool. By taking advantage of this fact double shades can be obtained upon mixed goods.

By mixing a weaker bath than the one indicated the cotton dyes up a dark green, and the wool acquires a dull and weak reseda shade. By a subsequent passage in bichromate these colours are changed upon the cotton to a bright black with a violet reflection, and upon the wool to a yellowish brown shade bordering upon olive, which is much in demand.

7. *Upon the use of Laval Catechu upon Woollen and Mixed Tissues.**

BY M. HOMMEY.

THE laval catechu manufactured by Poirrier has given us some special shades, which can be obtained from it more easily than by the usual mixture of dyestuffs. The action of different agents upon this substance has been described by M. Glanzmann, and as they are nearly the same for wool as for cotton we shall only speak of mixed goods.

Two observations may be made concerning these stuffs:—

(1.) The quantity of alkali which accompanies the colouring matter is a serious obstacle to its use for dark shades upon wool, so that we have found it impossible to obtain a dark chocolate or a black, the wool being in the first place acted upon and injured and the dark shades come out bad.

This inconvenience can be partly rectified by neutralising

*Bull. de la. Soc. Ind. de Rouen, iv., p. 266. See upon this so-called Laval Catechu, Textile Colourist, ii., p. 79.

with acetic acid the quantity of alkali which is not absolutely necessary, or by adding some acid salt to the bath, as, for example, bisulphate of soda, or even chloride of sodium (common salt) diminishes its caustic action.

But it is so easy to pass the limit of saturation, and consequently precipitate the colouring matter, that we preferred to give up the production of dark shades by this colour alone.

(2.) In those cases where bichromate is employed to raise the colour of the laval catechu upon white mixed goods of wool and cotton, the bichromate bath must be neither too strong nor too hot, for the yellow colour which the bichromate gives to the wool causes it to come up a different shade to the cotton.

For wool as for cotton the laval catechu can be used at a temperature of about 140° F. for weak baths, and 120° F. for stronger baths :

- (1.) Alone, to obtain greys and fancy shades of a special hue.
- (2.) Modified by acids and chrome to obtain fawn shades and fancies more or less dark.
- (3.) With metallic salts, such as the sulphates of iron and copper, for darker greys and various other shades.

It can also be used in mixture with other colouring matters; annatto has been mentioned ; the colour known as Coupier's blue can also be employed. A bath was prepared with 10 gallons of water, $\frac{1}{2}$ lb. of laval catechu, and $1\frac{1}{2}$ ozs. of Coupier's blue, and the cloth worked in it and afterwards passed in weak sulphuric acid, 6 parts to 1,000 of water, squeezed and washed. (The specimen in the text upon a mixed cotton and wool tissue shows a drab, pretty even, but somewhat darker on the cotton than on the wool).

Among the applications of this colouring matter we may mention those that can be made in dyeing cloth made from old wool (shoddy) containing bits of cotton ; the laval catechu enables us to obtain uniform shades, for it dyes the wool and the cotton at the same time.

(A sample of cloth is gummed in the text, which, though not quite even, is free from white specks).

Further, the action of the raising liquors, required to develop the shades of the laval catechu, can be pushed further, so as to change the original shade of the dye, and still the cotton points remain sufficiently covered to give a good result.

(This is illustrated by a specimen of cloth of a brown colour which had been raised in bichromate at a temperature of 185° F.)

This colouring matter can also be used to dye cotton rovings for after mixing, during the carding operations, with wool dyed by the same means or by other means yielding similar colours; the fastness of these colours enabling them to resist the operations which the mixed fabric has to undergo.

Specimens of felt, containing 30 per cent. of cotton, dyed by the laval catechu were shown to the Society, the colour of which had perfectly well resisted the carding and soaping.

8. *Upon the Tinctorial Power of the Leaves and Branches of "Lucée," and the Leaves of "Memecylum Tinctorium."*

THE two vegetable matters above have been recently examined by Messrs. Lamy and Benner, and reported upon to the Industrial Society of Rouen (see Bulletin of this Society for May and June, 1876). Of the Lucée, the English equivalent of which we do not know, it is said to be employed in Guyan for the black dye, and *Memecylum tinctorium* is used at Ceylon for dyeing yellow, and as a preparation in the Turkey red process. According to M. Lamy, the first contains tannin, and a small quantity of a yellow colouring matter, they give nearly the same results in dyeing as gall-nuts, but weight for weight are very much weaker. Mixed with garancine they seemed to have a less injurious action upon the purple than sumach or galls, but they stained the whites very much. Treatment with sulphuric acid as in making garancine from madder, gave a product not much differing from the original except that the yellow colour seemed to be more developed.

The same authority states that the leaves of *Memecylum tinctorium* behave in dyeing like quercitron bark, but are very much weaker, and he concludes that it is not probable that anything useful will be done with these products.

M. Benner made experiments independently upon the *Memecylum tinctorium*, treating it with sulphuric acid in the manner of garancine making. He also reports it as a very weak colouring matter, giving colours like quercitron, but requiring five times the weight to give similar shades. It may be useful, he says, in countries where sumach or quercitron are not obtainable, but cannot be profitably employed elsewhere.

9. *Upon a New Thickening Material.*

WE take the following from papers by M. J. J. Heilmann and M. J. Reber, read before the Industrial Society of Rouen. The thickening matter is a vegetable powder prepared from the algae of the French coasts, either alone or mixed with other substances, it is called French thao. It is probably the various proportions of the mixed substances which constitute the qualities Nos. 1, 2, and 3 of the material, the respective prices of which are 4 fr., 4 fr. 50 cents., and 5 fr. the kilogramme.

The French thao is in the form of a grey powder, mixed with yellow particles, of a strong smell, exciting to the nostrils, and resembling that of lichens. It dissolves in water by long boiling, and produces a transparent mucilage of a yellow colour, flowing freely when hot and somewhat less when cold. The yellowish colour is strongest in the No. 3, and less so in the No. 2. Upon cooling, the solution lets a considerable deposit subside, which renders straining or sieving necessary. The residue is gelatinous, and becomes horny when dried. Even after straining, the solution produces a fresh deposit after a time.

The mucilage does not become much thicker upon cooling,

nor take the form of a trembling jelly, same as the Haï-thao. On the contrary, it keeps its flowing character unless too strong.

When the French thao is mixed with cold water it forms lumps which, as before stated, only dissolve after a pretty long boiling. If, however, the cold mixture be made some hours in advance, the solution is effected quickly by heat, and is accomplished by raising to the boil.

It dissolves partially in cold water, producing a more colourless mucilage, but leaving a greater amount of insoluble matter than when dissolved hot.

The product is perfectly neutral. It dissolves completely and more easily in strong or diluted acids than in water. It is also soluble in alkalies. In both cases the solution is as thick as with water alone ; the solution in alkali is, however, more transparent, but at the same time more coloured.

When dissolved at the rate of $1\frac{1}{2}$ lb. per 10 gallons of water, it gives a tolerably thick liquid, which, however, is not strong enough for finishing purposes ; at $2\frac{1}{2}$ lb. per 10 gallons it does not give so much stiffness to cloth as $1\frac{1}{2}$ lb. of the Haï-thao. The feel of the cloth is nearly the same in both cases, but the French thao does not fill the fibres so well. The inconvenience already remarked with the Haï-thao of giving a colour to cloth is much more marked with the new product, and it is on that account unfit for weighting white calico. But it may be capable of rendering good service in finishing prints and lustrines, and as its thickness does not much increase by cooling there is no necessity to have it hot for finishing as is the case with Haï-thao.

The property which the French thao has of preserving its fluidity led to the idea of its being adapted as a thickening for colours in printing.

To try this M. Heilmann printed by machine a red from coralline, thickened with French thao at the rate of 3 lb. per 10 gallons, comparatively with three other reds of the same strength, one thickened with $3\frac{3}{4}$ lb. gum Senegal per gallon, the second with $3\frac{1}{8}$ lb. dextrine, and the third with a mixture of French thao and gum Senegal.

The colour from the thao was a little thicker than the others. It gave almost as clear and neat an impression as gum Senegal or dextrine. The mixture of gum and thao gave the worst results. Owing to the much smaller quantity of thickening matter present, the colour came out more beautiful, and fuller with the French thao.

An equally good result both by block and roller was obtained from ultramarine blue at $2\frac{1}{2}$ lb. of thao per 10 gallons when tried comparatively with the same colour thickened with gum Senegal at $3\frac{3}{4}$ lb. per gallon. The French thao being only partially soluble in cold water, the colour thickened with it resisted washing much better than the Senegal gum colour, hence probably there may be some advantage in using it to mix with albumen.

M. Heilmann left the question of the behaviour of this thickening with mordants to M. Reber, who is more especially acquainted with printing; he notes, however, an observation of M. Depierre, that this thickening mixes very badly with aniline violet, which he has confirmed by his own experiments. In conclusion, M. Heilmann says, that it does not appear that the French thao can be used as profitably for finishing goods as the Haï-thao.

M. Reber remarks upon this substance that it mixes with water like roasted starch, and that the solution becomes thicker by boiling; at the rate of $\frac{3}{4}$ lb. per gallon of water, heated to 150° F. and strained, it gives a paste which resembles a mixture of starch and gum tragacanth, but which is heavier, and not so gummy. Passed through a fine sieve a quantity of inert, insoluble matter is strained out, quite insoluble, and which when dry, amounts to 8 or 10 per cent. of the weight of the thao employed. The paste becomes more fluid by addition of 5 per cent. of acetic acid, which serves also to preserve it from fermentation, and from giving off a fetid smell.

The majority of colours and mordants used in printing can be thickened with the French thao, and the shades obtained are generally darker than when gum Senegal or dextrine is used for thickening, and may be compared with those given

by a thickening composed of mixed gum tragacanth and roasted starch (British gum). The colours thickened with this material have generally a weak consistence, wanting in body, and frothing easily during working.

The exceptional thickening power of the material may however, be probably put to good use in the cheaper kind of goods.

Thus, a thickening made with 1 lb. of thao at 5 fr. 25 cents the kilo. per gallon, will be cheaper than either tragacanth, gum Senegal, or a mixture of starch, paste, and tragacanth.

Mordants for purple, alizarine pink, and garancine catechu, thickened with the French thao gave satisfactory results, care having been taken to separate the insoluble matters.

Albumen colours which are too thin may be thickened with the thao.

As already stated, the worst feature of the French thao is the large quantity of insoluble matter in it, which cannot be wholly separated from the thickened fluid, and which, in most cases, would cause the "sticking in" of the colour in the engraving. A second important defect in it is the pasty nature and want of "gumminess" of the solution. Until these defects are removed, this substance cannot be expected to find a regular use as a thickener.

10. *Upon a New Class of Colouring Matters.*

A PAPER with this heading, by Mr. Charles Lauth, appears in the August number of the *Moniteur Scientifique*. The primary materials are the aromatic diamines obtained by reducing the nitrated derivative of the acetylic combination of the organic bases. Taking aniline, for example, first the acetanilide is produced, then the nitracetanilide and the nitraniline, and lastly the nitraniline is reduced by iron and acetic acid or by tin and hydrochloric acid; in the first case it is necessary to

add an excess of lime on the termination of the reaction and distil the mixture; in the second case a liquor is obtained from which the tin can be separated by zinc and the mixture directly employed to obtain the colouring matter. The novelty consists in introducing sulphur into the diamines; this can be done by heating them to a high temperature with sulphur, and the resulting product, in the case of phenylene diamine, yields, by oxidizing agents, magnificent purple-blue colours.

It is probably better and certainly quicker to produce the sulphuration and the oxidation by a single treatment. For this purpose the hydrochloric solution of the phenylene diamine is saturated with sulphuretted hydrogen and perchloride of iron added; the sulphur which is liberated in the nascent state combines with the base, and by continuing gradually to add the oxidizing agent the colouring matter is seen to form and eventually precipitate; it is collected on a filter, washed with water lightly salted to remove some impurities, then dissolved in boiling water and cooled, the product is thus obtained in a pure and beautifully crystallized state.

The following proportions were taken :—

For 20 grammes of hydrochlorate of phenylene diamine.	
Water saturated with sulphuretted hydrogen	4,000 c.c.
Hydrochloric acid.....	20 grammes.
Perchloride of iron, 10 per cent. solution...	500 c.c.

The new violet is a very beautiful colouring matter and gives very pure colours in dyeing, much more blue than the bluest shades of the *Violets de Paris*, and preserving their peculiar hue by artificial light.

In the dry state it is a dark brownish green, it is very soluble in pure water, but the smallest trace of foreign matter affects its solubility; the alcoholic solution is redder than the water solution and dichroic, the solution in alcoholic soda has a magnificent magenta-red colour.

Soda added to the solution of the violet gives rise to a brown precipitate which is apparently the base of the new colouring matter; ammonia gives a violet precipitate, as do

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the acids, but an excess of acid redissolves the precipitate. The acetic acid solution is violet, while the solution in the mineral acids is a pure blue colour; by diluting these solutions the colour is precipitated again.

Metallic salts give rise to violet precipitates which become soluble when the salts are removed by washing; chloride of zinc gives a bulky amaranth precipitate; chloride of sodium separates the violet from its solutions, but transforms it partially into a new violet matter insoluble in water; when the precipitation by salt is several times repeated a complete transformation takes place and the soluble colouring matter entirely disappears; boiling with solution of salt produces the same effect. Tannin forms with the violet a combination insoluble in water.

Reducing agents completely decolourize the solutions of this new substance; a few moments boiling with zinc powder produces this effect, but a simple agitation in contact with the air restores the original colour.

Oxidizing agents rapidly destroy the new colour.

The new colouring matter, like most of its congeners, is capable of yielding other colours by substitution; heated with aniline it gives a blue insoluble in water but soluble in alcohol; submitted to the action of aldehyde, iodide of methyl, &c., in the usual conditions it is changed into blues more and more of a greenish hue and of great purity, and presenting a novel property—that of being soluble in water and fixing upon fibres by simply dipping them in the solution; this property is interesting, for it is well known that the process of dyeing with the aniline blues requires precautions.

Mr. Lauth says his occupations do not permit him to pursue the study either scientific or practical of these new products, but he has satisfied himself that sulphur enters into their constitution, and he recalls the fact that several years ago he observed the presence of sulphur of constitution in the so-called aldehyde-green.

II. *M. Michel de Vinant on Dyeing, Printing, and Bleaching.**

IN continuing our extracts from M. de Vinant, we might give a number of other receipts for yarn dyeing, but on looking carefully over them there does not appear to be anything different in principle or method from the processes described in much older books, and we should imagine that this branch of dyeing was as well or better understood in England than in France. At the end of the section upon yarn dyeing there is a characteristic piece of M. de Vinant's writing which is worth translating for its own sake, as well as for shewing that operative dyers, the world over, have very similar opinions about the help they may get from science; he says:—"I repeat again, that by varying the proportions of colouring matters, dyeing is like a bottomless well as to variety of shades.

"I lay special stress upon dyeing cotton, as yarn or thread, because in that style we are most behind, and it is amongst the cotton dyers that I have met the least inclination for experiment. I have known numbers of men engaged in dyeing who, when I have spoken to them of an author who might be useful to them, have replied, 'Don't talk to me about chemists, they have never had any practice; they make experiments in a laboratory upon an ounce or two of stuff. But let them come to work over a tub, or over a pan; they will soon see that their style won't do.' Others say, 'I have tried this or that process from M. Chevreul's book, or some other, and I never got anything, or else the shade was a hundred miles away from what it should be.'

"It is quite useless to hint to them that they who practise the art and have the practical skill, ought to make another trial with a change of proportions and probably they would succeed; they will answer you, 'I have no need of him, I know more about dyeing than he does.'

* Continued from p. 73.

“With such feelings it is difficult for an art to make progress among working men, who wish that everything should be given to them, so to speak, cut and dried.”

M. de Vinant says that amongst woollen and silk dyers he has found more enlightenment and more desire to keep up with improvements.

Cotton Piece Dyeing.—We give some of the processes described by Vinant, not that they present much novelty, or that they are better, or even so good, as those with which English dyers are familiar, but they will probably shew some differences which may be of interest.

Black.—The damp pieces are padded twice in a mixture of equal parts of iron liquor at 9° Tw., and red liquor at 6° Tw., and left wet for twelve hours, being from time to time exposed to the air, the mordant is then fixed in warm silicate of soda, washed and dyed up in logwood, dried at a gentle heat without washing.

The finishing starch for black calico is made as follows :—

10 gallons weak logwood liquor.

½ lb. of fat.

5 ½ lb. of potatoe starch.

3 ½ lb. of white starch.

2 lb. sulphate of iron, at 1 ½ lb. per gallon.

Boil and use hot; then dry the goods in a hot room, and leave them exposed to the air for twenty-four hours.

Dahlia.—The calico in the humid state is padded twice in a warm logwood liquor at 4° or 5° Tw., leave on the roll twelve hours, then without washing pass cold in a solution of ½ lb. tin crystals in 10 gallons of water.

Another Dahlia.—Pass or pad three times in a catechu liquor made with 60 gallons of water, 6 lb. sulphate of copper, and 20 lb. catechu, with a little acetic acid if the water is hard; then pass in bichromate at 1 ½ lb. chrome to 60 gallons water, leave one hour and wash well; pass in logwood liquor at 4° to 5° Tw., twelve hours afterwards pass in solution of tin crystals, ½ lb. to 10 gallons of water.

Light Maroon or Chocolate.—Pass twice in peachwood or sapan liquor, at 4° or 5° Tw., and leave four hours; without

washing pass into the tin liquor same strength as above; leave one hour, wash, extract or squeeze, and pass in the same catechu liquor as in the last receipt, leave for six hours, and pass in the same bichromate liquor.

Aventurine, or Light Brown.—Pass twice in the same catechu liquor as above, and without washing into the same bichromate, leave two hours, wash and dry.

Cuir, or Leather Shade.—Dye aventurine first, pass twice in fustic at 4° or 5° Tw., leave for two hours and pass in the tin solution as above, leave one hour and wash lightly.

Crimson.—Pad the moist pieces in oxymuriate of tin, 8 lb. to 7½ gallons water, then without washing pass into carbonate of soda, at 1 lb. per gallon or 7° Tw., wash well and dye warm in red wood until a good shade is obtained; after dyeing, cool, and without washing pass through oxymuriate at 4° Tw., express well and pass again in the red wood, wash well and drain, finally pass through a weak red wood liquor, and dry without washing.

[To be continued.]

12. *Abridgments of Complete Specifications of Patents Recently Published.*

A.D. 1875, November 25th.—No. 4088.

ALEXANDER, EDWIN POWLEY. "Effecting the Carbonization of Vegetable Materials contained in Wool, Woollen Rags, or other Animal Substances." (*A communication from D. Michel.*) The acting agent is muriatic acid gas liberated by heat from the liquid acid in a close chamber heated to about 86° or 122° F. The wool to be acted upon is contained in wooden trays with wire gauze bottoms moving upon wheels in the upper part of the chamber. The goods may remain two or three hours exposed to the gas in the chamber and then withdrawn. "The vegetable matter contained in the wool or

other substances under treatment having been exposed on the carriage to a moderate heat and to the action of the said gas for a period varying from about two to three hours' duration, becomes friable, and loses all consistency, and by merely rubbing it between the fingers, it falls in the form of dust, whilst the wool, woollen rags, or other animal substances with which the said vegetable matter may be mixed, remain unaffected, and preserve their original colours."

A.D. 1875, November 26th.—No. 4108.

WILLANS, THOMAS BENJAMIN. "Finishing Woollen Fabrics." (*Provisional Protection only*). This patent refers to the elongating of cloths which have been shrunk by milling, and as inconvenience has been found to result from unequal shortening of pieces which could not then be submitted to the same stretching operations, the inventor simply proposes to measure the pieces by a measuring machine, and put those together which have suffered an equal contraction.

A.D. 1875, November 29th.—No. 4138.

CLARK, ALEXANDER MELVILLE. "Manufacture of Artificial Purpurine and other Colouring Matters." (*A communication from W. F. L. Grawitz.*) Oxyalizarine, or artificial purpurine is made by dissolving alizarine, either natural or artificial, in concentrated sulphuric acid, either hot or cold; nitric acid, to the extent of 26 per cent. of the weight of the dry alizarine, is then added, and the temperature of the liquid raised. The progress of the reaction is tested by taking a drop of the liquor and dissolving it in caustic potash. "If the colour resemble that of a red currant, without any tinge of violet, the operation is complete, but if not, a slight excess of nitric acid is added." "When the operation is terminated, the mass is run out in a thin stream into a considerable quantity of water. The oxyalizarine precipitates in flakes, and is then filtered and washed until the acids are completely eliminated, and afterwards dried if desired." Besides the oxyalizarine, the patentee describes the manufacture in a similar way of what are called nitroalizarines, nitroxylizarines, and chloroxyalizarines, of each of which there are three distinct compounds.

A.D. 1875, October 29th.—No. 3757.

SAUVEE, ALBERT. *A communication from Cesar Corron. (This invention received Provisional Protection only.)* The object of this invention was to apply machinery to "wringing skeins of silk or any other spun material, and separating the threads whereby those operations in the various stages of manipulation which precede and follow the dipping of the skeins in the dyeing vat, at present done by hand labour, are to be done by machinery." The invention cannot be described without a drawing.

A.D. 1875, December 2nd.—No. 4177.

ANDERSON MARK FRENCH and ROTHERHAM ALEXANDER "Improvements in Dyeing Silk and Cotton, and in preparing Silk and Cotton for the Manufacture of Ribbons and for other purposes." (*This invention received Provisional Protection only.*) This patent is for the use of gelatine or glue or other analogous material, such as isinglass, to be mixed with aniline or other dyes and the dyeing conducted in the usual way. "The effect of this treatment will be to impart a regular and even colour to the silk or cotton, and to prevent the colouring matter from striking in too quickly." The same materials are to be used for weighting silk "so as to fix the weighting material on the silk and for imparting to both silk and cotton an insoluble waterproof gloss, which much improves the appearance of the article and renders it easier to weave."

A.D. 1875, December 6th.—No. 4208.

UNDERWOOD GEORGE HILL. "Improvements in the treatment of Indigo for Dyeing and Printing." "This invention consists principally in the use of phosphorous for the purpose of deoxidising indigo for dyeing and printing, by which means most satisfactory results are obtainable." The following proportions may be used:—"1 lb. of pulp indigo; containing about 8 oz. of fair commercial indigo; 3 ozs. of amorphous (known also as red or granulate) phosphorous; one part of liquid caustic soda standing about 85° Tw., and 1 oz. of pulp lime." Besides amorphous phosphorous, common phosphorous dissolved in any of its

solvents, or phosphorous triturated in fatty or other suitable matters, and thus reduced to a fine state of division, may be used. After admixture the colour is ready for printing. "After printing and drying I pass the printed fabric, warp or yarn through an atmosphere of steam, and steam it in the ordinary way as practised by calico printers, and by this process the indigo becomes deoxidized or reduced to the white state on the surface of the textile fabric." "The cloth or yarn may be steamed by any of the ordinary methods well-known to calico-printers, but for cloth I prefer the following mode of steaming :—I take a perforated metallic cylinder open at both ends, having hooks attached, so that it can be suspended in the steam box ; over the cylinder I wrap about three folds of blanket, and then wind the printed cloth, along with a grey cloth, upon the cylinder (or the printed cloth alone without the grey cloth), and then cover the whole with a blanket and suspend it in the steam box to be subjected to the action of the steam." The goods may be steamed an hour, and after steaming washed in water or passed in weak acids. Claim is also made for reducing the indigo before printing, and for combining with it in either condition metallic oxides, such as oxides of lead or tin, so as to obtain compound colours by after treatments.

13. *British and Foreign Patents, from the Commissioners of Patents Journal, July 25th to Aug. 25th, 1876, inclusive.*

Colouring Matters.

1851. RICHARD SIMPSON, ARTHUR BROOKE, and THOMAS ROYLE, all of Greenford Green, Alizarine Works, Harrow, in the county of Middlesex, for an invention of "Improvements in the preparation of alizarine and other analogous colouring matters made from anthracine."—Dated 2nd May, 1876.—This patent has passed the great seal.
3270. JOHN GARRETT TONGUE, of the firm of Tongue and Birkbeck, Patent Agents and Engineers, of 34, Southampton Buildings,

Chancery Lane, in the County of Middlesex, for an invention of "Improvements in means and processes for obtaining colouring matters from cannel, anthracite, and other coals, applicable to various useful purposes."—A communication to him from abroad by Doctor Meusel, of Breslau, in the empire of Germany.—Dated 19th August, 1876.

175,829. WILLIAM H. FISH, of Pascoag, R.I., for "Dyes."—Application filed 31st January, 1876.—American patent.

Claim.—"The indigo-dye solution composed of indigo, zinc-dust, bisulphite of sods, caustic soda, and water, in, or about in, the proportions herein set forth."

40,158. A. POTEL, for an imported invention of "Employing alkaline silicates as a colouring element for jute thread."—Dated 2nd August, 1876.—(French patent, 16th May, 1876.)—Belgian patent.

The following are French patents.

112,332. JEANNOLLE, of Levallois-Perrett, for "A process for substituting aniline for indigo in dyeing vegetable or animal fibres, woven or not."—Dated 7th April, 1876.

112,561. MAZET, of Clermont Ferrand, for "Manufacturing black colour."—Dated 4th May.

112,636. POTEL, of Armentières, for "Using silicates on jute thread as a colouring element."—Dated 10th May, 1876.

Apparatus and Machinery for Processes of Dyeing and Printing.

670. JOSEPH FIRTH, of Leeds, in the county of York, for an invention of "Improved apparatus for use in dyeing fabrics indigo blue."—Dated 17th February, 1876.

717. JAMES CHADWICK, of the Spring Brook Print Works, Chadderton, in the county of Lancaster, for an invention of "Improvements in dyeing and printing textile fabrics."—A communication to him from abroad by James Harley, of Lowell, Massachusetts, United States of America.—Dated 21st February, 1876.

1036. LÉON GODEFROY, Son, of the firm of Vve. L. Godefroy and Son, of Puteaux, near Paris, Printer, for an invention of "An improved process of printing or ornamenting woollen or other similar textile fabrics."—Dated 10th March, 1876.

The above patents have passed the great seal.

1654. WILLIAM MORGAN-BROWN, of the firm of Brandon and Morgan-Brown, Engineers and Patent Agents, of 38, Southamp-

- ton Buildings, London, and 13, Rue Gaillon, Paris, has given notice to proceed in respect of the invention of "Improvements in the manufacture of ornamental textile fabrics."—A communication to him from abroad by Samuel Barlow, of Lawrence, Massachusetts, United States of America, Color Master.
2748. JAMES MORTON, Manager to Messieurs William Stirling and Sons, of Cordale and Dalquhurn, Turkey-red Works, in the county of Dumbarton, North Britain, has given notice to proceed in respect of the invention of "Improvements in preparing woven fabrics and yarns of cotton or other vegetable fibres for being dyed or printed."
3018. JEAN PERINAUD, Chemist, and JUSTIN MARCHAL, Dyer, both of Paris, France, for an invention of "A process of supplying dyed silk fabrics."—Dated 26th July, 1876.—Provisional protection has been granted.
3248. ALEXANDER BROWNE, of the firm of Browne and Company, Patent Agents, of 5, Southampton Buildings, Holborn, in the county of Middlesex, for an invention of "A new or improved mode and means for producing paintings on all kind of textile and other fabrics."—A communication to him from abroad by Messrs. Gustave Cleis and Company, of Montrouge, France.—(Complete Specification.)—Dated 18th August, 1876.
2564. THOMAS PICKLES, of Heckmondwike, in the county of York, SAM SMITHSON, of the same place, and CHARLES HENRY PICKLES, of the same place, Dyers, for an invention of "Improvements in apparatus employed in dyeing fabrics."—Dated 28th July, 1873.—This patent has become void.
2703. THOMAS FOX, and CHARLES HENRY FOX, of the firm of Fox, Brothers, and Co., of Wellington, in the county of Somerset, for an invention of "Improvements in machinery for dyeing piece goods."—Dated 15th August, 1873.—The stamp duty of £50 has been paid upon this patent.
22. A. CHIFFRAY, of Maromme, France, for "Improvements in his machine for printing both sides of fabrics with one or several colours, and for obtaining at the same time ribs suitable to such colours, as patented 9th December, 1872."—Dated 17th February, 1875.—Wurtemberg patent.
86. F. BARTELS and Dr. E. FREISSE, of Göttingen, for "A process of dyeing and colours belonging thereto."—Dated 2nd June, 1875.—Wurtemberg patent.

165. F. FLINTSCH, of Offenbach, for "A dyeing machine."—Dated 29th September, 1875.—Wurtemberg patent.

175,554. OSCEOLA CURRIER, of Newark, N.J., for "Machines for printing fabrics."—Application filed 29th November, 1875.—American patent.

Brief.—"The frame is raised and lowered by means of a pinion on each end of a shaft gearing with a rack attached to the sliding bars. The pressure of the printing-roll is graduated by the weight."

Claim.—"The hangers C¹, C², the sliding bars Y, frame F, each constructed and operated in combination with the printing-roll E, as and for the purpose set forth."

174,891. SAMUEL BARLOW, of Lawrence, Mass., assignor to Pacific Mills of the same place, for "Processes of manufacturing ornamental textile fabrics."—Application filed 10th March, 1876.—American patent.

Claim.—"The art of producing figured cloth by weaving of vegetable fibers the portions to be stained or printed, and of animal fibers the portions to be left unstained or unprinted, and then printing the woven fabric with aniline black, and cleansing it substantially as described."

Engraving, Drying, Bleaching.

364. THOMAS NIXON, Pentagraph Engraver to Messrs. John Orr Ewing and Company, of Alexandria, in the county of Dumbar-ton, North Britain, for an Invention of "Improvements in pentagraph engraving machines."—Dated 29th January, 1876.—This patent has passed the great seal.

2956. JOSEPH KEIM, of Tharm Alsace, Allemagne, for the invention of "Improvements in machinery for stretching and drying textile fabrics."—Provisional protection has been granted.

97. V. VAN BARLE, of Worms, for "Bleaching fibrous substances."—Dated 3rd June, 1875.—Wurtemberg patent.

112,481. DECOUDUN and Co., for "Improvements in hot-air drying rooms for linen and tissues."—Dated 19th April, 1876.—French patent.

2489. MATTHEW CLARK, of Alexandria, in the county of Dumbar-ton, North Britain, Turkey-red Dyer and Printer, for an invention of "Improvements in and connected with drying stoves employed in the manufacture of Turkey-red yarns and woven fabrics."—Dated 19th July, 1873.—This patent has become void.

Hanks and Skeins.

3089. SIDNEY ELLIS, of the Newarke, in the town and county of Leicester, has given notice to proceed in respect of the invention

of "Improvements in machinery or arrangements for washing, dyeing, and sizing yarn or thread in the hank."

112,285. BOULIEN, Brothers, and CHARLON, of Lions, for "A machine for beating and washing filaments in skeins."—Dated 22nd April, 1876.—French patent.

112,654. GILLET and Son, for "Improvements in machines for washing filaments in skeins."—Dated 12th May, 1876.—French patent.

Wool Treatments.

2294. WILLIAM PHILLIPS THOMPSON, of the office for patents, 6, Lord Street, Liverpool, in the county of Lancaster, Consulting Engineer, for an invention of "Improvements in apparatus for Washing wool and other similar fibre."—A communication to him from abroad by Frederick G. Sargent, of Graniteville, Middlesex county, Massachussetts.—Dated 31st May, 1876.

2477. SAMUEL BAMFORD, of Royton, in the county of Lancaster, for an invention of "Improvements in the method of treating mixed woollen fabrics for the purpose of separating the wool from any other fibrous material employd in the manufacture of such fabric."—Dated 15th June, 1876.

2916. EDWIN POWLEY ALEXANDER, of 14, Southampton Buildings, in the county of Middlesex, Consulting Engineer and Patent Agent, for the invention of "Improvements in the treatment of woollen and silk fabrics and other goods composed of animal products with a view to the removal of any vegetable substances contained therein; also in the apparatus or means employed therefor."—A communication to him from abroad by Daniel Michel, of Paris, in the republic of France, Woollen Waste Manufacturer.—Provisional protection has been granted.

2947. CHRISTOPHER WEBB SMITH, of Barnwood, near the City of Gloucester, Chemist, for the invention of "Improvements in and apparatus for scouring or cleansing woollen cloth, yarns, and wastes, and in recovering valuable products from the materials which have been used in conducting the said scouring or cleansing."—Provisional protection has been granted.

2485. GODEFROY SIRTAINÉ, of Verviers, in the kingdom of Belgium, Industrial, for an invention of "An Improved method of cleansing wools from burr and seeds, and for the disintegration of vegetable matters generally."—Dated 19th July, 1873.—The stamp duty of £50 has been paid upon this patent.

- 175,258. F. G. SARGENT, of Graniteville, Mass., for "Wool-washing machines."—Application filed 23rd December, 1875.—American patent.

Brief.—"Within a tank is a curved table having rigid teeth, over which moves a reciprocating frame with pivoted teeth, arranged to rise and fall by means of pitman, crank, and a weighted arm. An injector with pipes for conveying water to the tank, and rollers for squeezing the water from the wool when washed.

Claim.—"1, in combination with the curved table C, provided with the rigid teeth *b*, the frame E, supported by a pivoted arm or arms F, and provided with the pivoted teeth *c*, substantially as shown and described. 2, in combination with the table C and the reciprocating toothed frame E, the toothed frame M, hinged to the frame E, and arranged to rise and fall, substantially as shown and described. 3, the combination of the frames E and M, pitman I, crank K, and link N, substantially as shown. 4, in combination with the pitman I and link N, arranged and operating as described, the screw *a*. 5, the combination of the frame E, arms F, rock-shaft G, and the weighted arm H, as shown. 6, in combination with a wool-washing machine, the injector S, or its equivalent, provided with the perforated pipes T and U, or either of them, arranged to deliver a spray upon top of the fiber as shown and described. 7, in combination with the injector S, or its equivalent, the pipes T and U, or either of them, and the pipe W, arranged as shown, whereby the water may be withdrawn from the bottom of the tank and delivered upon the fiber, as described. 8, in combination with the body A and rolls B, the screen P, arranged in the body below the rolls, but above the liquor-level, as and for the purpose described. 9, in combination with the body A and rolls B, the inclined table C, having the concave lower and convex upper end, and devices, substantially such as shown, for feeding the fiber from the body upon the table to the rolls. 10, in a wool-washing machine, a table C, having its upper end made of a convex form, substantially as and for the purpose described."

195. E. GESSLER, jun., of Metzingen, for "A machine for washing dyed wool."—Dated 15th December, 1875.—Wurtemberg patent.
196. E. GESSLER, jun., of Metzingen, for "A machine for washing raw wool."—Dated 15th December, 1875.—Wurtemberg patent.
- 40,017. D. MICHEL, a Patent of Improvement for "Carbonizing vegetable matter in wool and woollen rags."—Dated 14th July, 1876.—(Original Patent, 25th November, 1875.)—Belgian patent.
- 40,087. V. and A. and J. TRIBOLLET, of Brussels, for an imported invention of "Scouring wool and extracting the substances contained in suds."—Dated 24th July, 1876.—(French patent, 15th September, 1875.)—Belgian patent.
- 112,369. RAVEL, of Barrême, for "Improvements in his wool-

washing machine called 'Eiro-plunther,' as patented 16th April, 1864."—Dated 25th April, 1876.—French patent.

- 112,385. DELAMERE, jun., and Co., of Elbeuf, for "Chemical cleaning of woollen tissues by the dry way."—Dated 21st April, 1876.—French patent.

Finishing Processes.

844. LUKE SMETHURST, Presser, SAMUEL SHAW and THOMAS SHAW, Manufacturers, all of Holywell Green, near Halifax, in the county of York, for an invention of "Improvements in or applicable to machinery or apparatus used in the pressing of woven or felted fabrics."—Dated 29th February, 1876.—This patent has passed the great seal.
1118. JOHN BROWN, Dyer and Finisher of Fustians, WILLIAM DEAN, Overlooker, and ARTHUR ORRAH, all of Huddersfield, in the county of York, have given notice to proceed in respect of the invention of "Improved apparatus for cutting cotton, woollen, silk, or other pile fabrics."
3324. JOHN STEVENSON KERSHAW, of Littleborough, in the county of Lancaster, for an invention of "Improvements in apparatus for stretching woollen or mixed woollen and cotton cloths, which apparatus is to be used in conjunction with 'tentering' machines for drying woollen cloths."—Dated 24th August, 1876.
- 112,824. LALOUEL DE SOURDEVAL, for "Scouring and washing rags and filamentous and textile substances by means of sulphuret of carbon, hydrocarbons, &c., and apparatus employed therefor."—Dated 10th May, 1876.—French patent.
- 40,108. J. PIERNAUD and J. MARCHAL, for "Smoothing silk fabrics."—Dated 26th July, 1876.—Belgian patent.
2655. THOMAS ROBINSON, of Castleton Lodge, Leeds, in the county of York, Gentleman, for an invention of "Improvements in machines for raising woollen cloth, commonly called 'gigs.'"—Dated 7th August, 1873.—This patent has become void.
3127. JOSEPH TOWNSEND, of Glasgow, in the county of Lanark, North Britain, Manufacturing Chemist, for the invention of "Improvements in damping and preserving vegetable substances and vegetable and other textile materials and fabrics," bearing date the 21st day of November, 1862.—Application for a grant of prolongation of this patent is about to be made.

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*I. Notes upon Aniline Black.**

BY M. G. WITZ.

As soon as I became acquainted with the curious properties of vanadium as described by M. A. Guyard, I sought to obtain some of its compounds, which were however only to be found in a few scientific collections. Having verified the accounts of the action of this metal upon mixtures of chlorates and salts of aniline, I proceeded to apply the phenomena to dyeing cotton skeins black. This perfectly succeeded upon the small scale, shewing that the oxidation was considerably forwarded by the concentration of the liquors by drying, and correspondingly retarded when the solutions were diluted.

Having also observed that the action did not commence suddenly, but in a manner almost insensible at first, becoming gradually more rapid, and arriving at completion in a period of time varying with the quantity of metal present, this quantity being always very small, I took advantage of these favourable characters to apply the same method of formation of the black in colours thickened for printing.

In a series of successive trials in which the proportion of vanadium salt was added in decreasing geometrical progression, I determined the exceedingly small quantity of metal which sufficed to bring about the oxidation of the aniline. I

* Condensed from the paper read by the Author to the Industrial Society of Rouen, August 4th, 1876. Bulletin of the Society, iv., p. 340.

operated carefully by printing with the finger, and without contact of copper or any other metal, and with salts as pure as possible.

When pure salts (of aniline?) were replaced by ordinary commercial preparations of the best quality, the oxidation was even more easily effected, which leads to the supposition that a part of the good results obtained in practice may be attributed to certain impurities of an unknown nature present in them; the presence of iron in the hydrochloric acid used on the large scale and thus indirectly introduced in the other products may also have contributed to the result observed.

I finally arrived at a point where the proportion of vanadium employed in colours for printing became so exceedingly low that it should be reckoned by so many parts to *one hundred thousand* parts of aniline salt; and further, I was convinced that in printing it was impossible to exceed in any considerable degree these feeble doses without danger of destroying the thickened colour.

Statements so astonishing should be proved so as to admit of no question, and upon this occasion I may be permitted to enter into some necessary details, for aniline black is a colour not only of great value, but of great delicacy; there is scarcely any other colour which demands so much care or which calls so largely upon the skill of the chemist.

After my experiments upon the small scale I found no difficulty in working upon the large scale so as to dispense with the use of the sulphide of copper paste. On the 18th of February, 1876, I printed a considerable number of pieces which were sufficiently oxidized by twenty-four hours' ageing in the rooms regularly used for ageing aniline blacks. These were the first pieces printed in France or elsewhere, except in England, and specimens of them were exhibited at the time. At the present day I am probably the only one who prints exclusively with vanadium, without using copper or any other metal.

The characters of the black, its beauty and stability being known, there only remained to study the slight variations necessary to follow with different goods. For that purpose I

printed several hundred pieces, changing within narrow limits the proportion of vanadium. The rapidity of oxidation was always found to be in relation to the quantity of vanadium employed, a property which is of great value in practice.

One part of vanadium to 135,000, or 270,000 parts of muriate of aniline gives a colour for printing which is oxidized in a few days at a temperature of 77° F.

With 1 part to 337,000 parts of aniline salt the action is still sensible, the same colour without vanadium giving a very imperfect result, even after six days' exposure in the ageing room.*

Practically, the proportion of 1 to 67,000 of the weight of muriate of aniline may be adopted for colours containing $12\frac{4}{5}$ oz. of muriate of aniline per gallon of colour. I consider it well not to go far from this proportion.

The proportion which I have regularly used, both for block and roller, differs but little from the above, it corresponds with 0.0013 grms. of vanadium for a litre of colour weighing 1,100 grms. or about 1 part to 850,000 parts by weight of the thickened colour.†

For a colour containing $12\frac{4}{5}$ oz. of muriate of aniline per gallon, the amount of metal is 1 to 61,700 of the amount of

* In experimenting with pure materials, boiling and cooling the colour in a porcelain vessel and printing with the finger upon white calico well purified, that is avoiding all contact with metals, there can be observed a commencement of production of aniline black which is not owing to the presence of copper. By an inverse experiment it is easy to shew that any accidental traces of the metal present have nothing to do with the formation of the black; a quantity of *copper* in the state of sulphate was added representing $\frac{1}{1000}$ of the weight of the aniline salt, no increase of oxidation could be observed, the thickened colour underwent no change in two days. The same proportion of *vanadium*, on the contrary, gave a very dark black, and even decomposed the colour in less than a single day. This partial formation of black from pure materials may possibly be owing to the presence of some unknown active bodies, or may perhaps be attributed to the influence of atmospheric ozone.

† It is difficult to give exact equivalents in English weights and measures for these quantities. One gallon of aniline black colour, with starch thickening, may weigh say 11 lb. or 770,000 grains, for this quantity the proper weight of vanadium, according to the above proportion, would be nine-tenths of a grain; or, 1 oz. of vanadium would suffice for 4,829 gallons of colour. A practical method of adding the vanadium is given further on. These weights of vanadium are to be understood of the metal and not of the salts.—*Ed.*

muriate; taking the muriate of aniline as containing $\frac{11}{16}$ of its weight of aniline, the proportion of metal to pure alkaloid is as 1 to 42,500.

The quantities of vanadium at first used were still less than those just given, which were adopted to prevent the occurrence of a too tardy oxidation, or an incomplete oxidation in the case of certain designs or delicate combinations.

In two or three days' ageing at about 77° F. dry, and 68° F. wet bulb thermometer, the colour is perfectly raised, and then finished off in the usual way.

The use of sulphide of copper paste has been completely given up, as we have found a real advantage from vanadium by obtaining quicker and more perfect results; the coppering of the steel doctors never happens, and the engraving is not acted upon, and what is more remarkable, by using certain precautions, the thickened colour can be kept good for an indefinite period, that is to say can be preserved without any noticeable change for several weeks, a thing which was previously impossible.

With all these advantages the use of vanadium is eleven times cheaper than the sulphide of copper paste, as appears from the following calculation:—

One kilo. of aniline in the old black colour required 550 grammes of sulphide of copper in paste, costing about 55 centimes, and containing 100 grammes of metallic copper; while for the same quantity of aniline, 0.055 grammes of vanadate of ammonia, which can be obtained for less than 1 franc per gramme, costing say 5 centimes, replaces the above quantity of copper perfectly well in practice.*

The vanadate employed is equivalent to 0.024 of metal, which in this example shews it to have an action 4,200 times more powerful than copper.

Apparently any of the soluble vanadium compounds can be employed since the contact with chloric acid brings them all to their maximum of oxidation, but preference should be

*The price of vanadium salts in June, 1876, was twenty-one shillings per ounce.

given to those compounds which are soluble and characterised by a distinct form and colour.

The bivanadate of ammonia which is in brilliant orange-coloured crystals, unchangeable in air, seems the best salt to use. The anhydrous perchloride of vanadium is a liquid difficult to manage, it fumes strongly and has a great attraction for water. Vanadic acid and the vanadates of ammonia or soda are to be found in commerce, but these salts being devoid of crystalline form it is important to be certain of their actual worth. The comparative amount of vanadium in its principal compounds according to the latest researches is as follows :—

The chloride of vanadium is a dark red liquid, fuming strongly in the air, and producing a violent action upon water, it cannot contain more than 29 per cent. of vanadium, or 3.45 parts contain 1 part of metal; it was this compound which we used in our first experiments. The vanadate or meta-vanadate of ammonia is a heavy, dull yellow powder, and contains 43.6 per cent. of metal, or 2.3 parts equal 1 part metal.

Lastly, the bivanadate of ammonia which has no water of crystallization, contains 49 per cent. of vanadium, or 2.04 parts contain 1 part metal. This salt, the amount of vanadium in which can be readily ascertained, is perhaps to be preferred to the other vanadates, on account of its external appearances. There is a trivanadate of ammonia obtained in large hydrated crystals of a splendid red colour by acting upon the bivanadate with acetic acid; it is much more soluble than the bivanadate, but less permanent, losing ammonia and water at slightly elevated temperatures.

The alkaline vanadates are in general difficult to dissolve in water, it is recommended to treat them with warm hydrochloric acid, diluted with an equal volume of water, and to add slowly and with agitation either alcohol, wood spirit, or glycerine; these substances reduce in a short time the pulverent and insoluble vanadic acid into vanadous chloride which is very soluble. The following proportions may be employed :—

3 parts of vanadate of ammonia.

12 to 15 parts hydrochloric acid at 33° diluted
with its own volume of water.

1 part white glycerine at 46° Tw.

2 parts water.

After solution, water is added in such quantity that the resulting liquid shall contain 1 per cent. of pure vanadium, *i.e.*, 100 oz. of solution contain 1 oz. of vanadium, the liquid is clear and of a beautiful bright blue colour with a greenish hue. For use, this solution is preserved in small bottles containing 100 cubic centimetres (about $3\frac{1}{4}$ ounces); this avoids the loss from evaporation which would be caused by the frequent measuring of small quantities, which are for each occasion withdrawn by means of a graduated pipette.

The quantities of vanadium to be added to aniline colours vary in general in an inverse proportion to their strength, that is, in proportion to the aniline they contain; and further, according to the temperature or the time which can be given in ageing.

The facility of proportioning the quantity of vanadium so as to obtain at will a colour which ages up quickly or slowly, is one of the remarkable advantages of this class of colours.

If, for example, it is known that 3 measures of the solution of vanadium being added to 20,000 measures of black causes the colour to be developed in twenty-four hours in ageing rooms at a temperature of 77° F., then $2\frac{1}{2}$ measures of solution will give a colour requiring two days' ageing, and 2 measures a colour requiring three days, and so on for longer or shorter periods.

If the ageing rooms are kept at a higher temperature the proportion of vanadium may be reduced in accordance.

The strongest colours, as previously stated, require the smallest amount of vanadium. Thus in using $\frac{9}{10}$ lb. of aniline salt per gallon instead of $\frac{8}{10}$ lb. the proportion of vanadium indicated above would be too great, and should be diminished by about one fourth. The ratio then becomes as 1 of vanadium to 93,000 of aniline salt, or 1 to 64,000 of aniline oil,

and the cost is $16\frac{1}{2}$ times less than that of the sulphide of copper paste.

It is probable that the development of very rich blacks, say at 1 lb. of aniline per gallon, part of which is in the state of chlorate of aniline, does often take place without addition of any metallic salt, but the ordinary colours made with muriate of aniline cannot be developed without the presence of a trace of either vanadium or copper.

The very small quantity of the vanadium solution required is always made to the cooled colour, and just before the final straining; no irregularity of distribution of the vanadium has ever been observed when operating in this manner.

There is no more elegant process in our manufacturing operations than this, and the constant repetition of it does not prevent a feeling of astonishment that as a final operation in making up a tubful of colour, a few drops, carefully measured, of a metallic solution must be added; or further, that if the weather be warm, some even of these few drops must be kept back, and yet this is exactly what is done.

The nature of the thickening is well known to exercise a remarkable influence upon the production of aniline black; the darker varieties of roasted starch (dark British gum), and particularly dextrine and gum, give blacks much slower to oxidize than thickenings of starch or the lighter kinds of roasted starch (light British gum); these former thickenings cannot be employed along with sulphide of copper because it is too feeble in its action. If for certain fine patterns it is desirable to have aniline black thickened with gum or substitute, the black can be raised only by using about twenty times as much vanadium as with starch thickening, and giving three days' ageing.

After the preceding observations it would be superfluous to give any formal receipts, I have chiefly endeavoured to detail the best methods of replacing the sulphide of copper in general cases; it will not be difficult to obtain good results in any particular case.

It is well to observe that whatever kind of aniline salt be employed, whether nitrate, muriate, or mixtures of both, the

black which is obtained by printing is absolutely the same black and of the same intensity. We had, in conjunction with our honoured colleague, M. J. Reber, previously assured ourselves of this fact by experimenting upon pure solutions in a state of perfect neutrality. From its cheapness, the muriate or hydrochlorate of aniline is always to be preferred. The cost is considerably increased if instead of this salt aniline saturated by two equivalents of tartaric acid be employed, even when the bitartrate of potash which separates is collected; a portion of bitartrate of potash remains in solution in the colour where it plays the part of a real preservative salt, for it helps to prevent the hydrochloric acid set free in the ageing from attacking the delicate fibres of the cotton, and from dissolving any mordants which may be printed in conjunction with the aniline black.

There remain some modifications to be spoken of which may be considered as improvements of the ordinary aniline black colour.

The sulphide of copper paste being of a dark colour, and used in rather a large proportion in the thickened colour, sightens it sufficiently for the purposes of the printer; this is not the case in using vanadium, along with which some sightening must generally be used. I recommend for this purpose the methylaniline violet, or violet de Paris (for example the quality No. 145), of which 2 or 3 parts added to 10,000 of colour make it dark enough to be seen in printing.

The great advantage of this sightening (the violet de Paris), is that it serves as a reagent to indicate the state of acidity of the aniline salt used, and so to permit the necessary correction for the neutralization of the excess of acid which always exists in the commercial aniline salts. For purpose of the neutralization, rectified aniline oil can be added by small quantities at a time to the sightened colour until the bluish shade of the violet is turned to a fine reddish-violet hue; when this point is hit, the colour is certain to be in a state which will keep well and will not act upon the steel doctors when printing.

If too much aniline oil be added, the only harm done is to

keep back the oxidation and development of the colour after printing, which will only take place after the excess of aniline has volatilized away from the cloth. This sightening also shews clearly if the cloth has been too much heated in drying after printing, for the greenish-blue colour which is produced in this case is quite distinct from the colour which results from a moderate and proper amount of drying.

The change of shade in the violet sightening in the thickened colour serves also to point out changes in the degree of acidity or other decompositions which may be gradually taking place either by heat or other causes in the colour.

I calculate that $\frac{1}{2}$ to 1 part of free aniline oil in 1000 parts of colour is very suitable for roller printing when the temperature is not too high, and as the ordinary crystallized muriate of aniline of commerce generally contains from 1 to 3 per cent. of acid in excess, it is not difficult to estimate beforehand about what proportion of aniline oil should be added to the colour.

But commercial aniline oil is not of uniform quality, it is often impure and requires a long chemical examination to ascertain its real nature; and as, further, the use of the crystallized salts of aniline for black is causing the oil to take a secondary place in manufactures, it is advisable to endeavour to work without it.

Ordinary strong ammonia, bulk for bulk, can be advantageously used instead of aniline oil to neutralize the acidity of the colour. When it is added to the colour it sets some aniline free, which answers the purpose perfectly well, while there is at the same time formation of a quantity of salammoniac, which salt being in considerable quantity in the colour already can have no marked influence upon it.

Salammoniac, which has been considered from the commencement as an indispensable ingredient in the aniline blacks with copper salts, can be omitted without any inconvenience in the vanadium black, at least when the ageing is of a suitable degree of humidity, for the salammoniac does not appear to play any other part than an hygroscopic agent in the colour. The complete suppression of salammoniac in

aniline black may be of some importance in nitrate of aniline colours which are printed in combination with lead salts, since any inconvenience in the printing which might arise from the formation and precipitation of chloride of lead would be avoided.

It may be asserted with confidence that the vanadium black answers well for all styles of printing. It is perfectly good for steam styles after the black has been developed by ageing, and also for styles with white and orange resist, which can be worked without difficulty.

The sulphide of copper can therefore be completely dispensed with, and with it will disappear all those drawbacks arising from its easy transformation into a soluble salt of copper, causing the steel doctors to be corroded, hastening the decomposition of the colour as well as all the trouble of its preparation and keeping.

We cannot, however, speak of the displacement of sulphide of copper in the preparation of aniline black without paying a well-earned tribute to this ingenious chemical idea which has rendered such important services to industry. At the time when M. Charles Lauth advised in 1864 the employment of this material, the difficulties of printing aniline black appeared well nigh insurmountable, and until the introduction of vanadium, the dictum of M. Camille Koechlin that "without sulphide of copper aniline black would have been an impracticable colour" remained perfectly true.

The number of pieces which, thanks to the introduction of the sulphide, have been printed in various countries may be counted by millions. It is owing to this happy idea that so many different styles of prints of a fast and solid character have been produced, and so much general progress in many ways has been accomplished within the past dozen years. The discovery of aniline black may be looked upon as probably the most fertile and valuable which has been made for many years, and as the one which has most contributed to the prosperity of calico printing, and this in the midst of many wonderful inventions which have come to light in the same space of time.

But even at this day a reference to the original authorities shew that the improvements are nothing but simple variations of the first process as discovered by Lightfoot and perfected by Lauth. (See Schützenberger, i., p. 516; and Dict. de Chimie de Wurtz, i., p. 326.)

Some observations ought to be made relative to the proportion of chlorate which should be used to the aniline in the thickened colours, for it appears to me to be a very important point in practice.

The early receipts for aniline black for printing contained too little chlorate of potash. The aniline was in excess and there was loss of it; at the same time it is probable that the black was never sufficiently oxidized, and was sensitive to the influence of the weakest acids.

By using a quantity of chlorate of potash amounting to one half the weight of the muriate of aniline, a proportion recommended by M. A. Muller, of Zurich, from laboratory experiments, it was found in practice that the chlorate was in excess, for while this latter is an anhydrous salt and constant in its composition, the aniline salt on the other hand contained an uncertain quantity of water besides impurities which affected its equivalent weight. Now the presence of an excess of chlorate is very objectionable; thus after the complete development of the black in the vanadium process, the metal continues to decompose the chloric acid, and when the oxidation is not arrested at the proper time it may act first in destroying and burning the aniline black with which it is in immediate contact, and secondly by emitting oxidizing vapours which give rise to light black stains when they meet with any aniline in the air surrounding pieces just printed; sometimes slight markings off are observed upon the white folds close to the colour, which have to be taken out by steam clearing.

M. C. Lauth took the proportion of chlorate of potash as 43.7 for 100 of muriate of aniline. I have found by practical experiments that 41.7 of chlorate of potash for 100 of muriate

of aniline is a good proportion. It is easy to calculate the corresponding quantity of any other chlorate.

In this paper we have barely glanced at other aniline blacks than those of the medium strength, which are the most commonly employed. The strong blacks which are employed for certain shallow engravings and for special combinations present still more remarkable features with respect to the small quantity of vanadium required for their development, since it is necessary to reduce the quantities given for the ordinary blacks.

It is, however, desirable to recall attention to the fact that the proportions of vanadium adopted, and which form the basis of the calculations in this Note, have nothing of an absolute nature in them, and that they may be varied considerably according to the conditions of procedure or the object aimed at. We only say that the proportions above given are those which were most suitable in the particular circumstances under which the trials were made, and we may add that in working on the large scale the results have fully justified the expectations which were entertained.

The quantities mentioned are for a moderately strong colour, as well as for a lower heat and longer ageing that is employed in some other places. It will be found by trial that there is generally an advantage in using the smaller quantities. The development of the black is completed in about two days at a temperature maintained constantly at from 77° to 86° F., with 9° or 10° difference between the wet and dry bulb thermometer. In this way there is no observable tendering of the tissue, the black is intense and comparatively little acted upon by the ordinary agents which tend to turn it green, the finest lines in the printing come out clear and neat, shewing all the details of the engraving, and lastly while the colour keeps well its price is not high. These are the considerations which have induced us to keep to the quantities we have given.

The black from aniline had been already introduced into so many different kinds of work that it is probable the vanadium

colours will not extend the bounds of its application; without offering any really different effects, its use presents new resources in economy and facility of application. For similar reasons products which have hitherto been known only to scientific men and of the greatest rarity enter into practical consumption notwithstanding their seeming costliness. Instead of storing up bulky quantities of sulphate of copper, of sulphur and of soda, for the purpose of making the black by an intermediate preparation which is preserved with difficulty in the state of a wet paste, the printer may in future have a few small phials containing a stock of vanadium sufficient to make aniline black for a whole season.

As a matter of curious calculation of the almost infinite divisibility of matter, vanadium black offers a good illustration; one gramme of it gives colour enough to print about 13,000 square metres of calico, and when the small portion of this calico which may be measured under a microscope of moderate power is taken into consideration and looked upon as containing a portion of vanadium, it is seen that the gramme weight of vanadium is divided into a number of parcels which may be represented in figures by unity followed by sixteen cyphers.

2. *Mr. W. H. Perkin upon Artificial Colouring Matters.*

THE following extracts from the address of Mr. W. H. Perkin, F.R.S., the President of the Chemical Section of the British Association, delivered at Glasgow in September, are of interest from several points of view, historical, practical, and theoretical. It will be seen that Mr. Perkin desires to impress upon chemical manufacturers and others the importance, if not the necessity, of cultivating and encouraging a spirit of original research with regard to the subjects in which they are mainly interested. At the outset he refers to the complaints of the

comparatively small number of original investigations which are communicated to the scientific literature of this country, but he shews that there has been a greater activity shewn of late years, and that the number of original papers read to the Chemical Society of London was three times more numerous in 1875 than in 1872. After referring to the handsome bequest of £6,000 which Mr. T. J. Philipps Jodrell has placed at the disposal of the Royal Society for the encouragement of research in physical science, he says:—

“The employment of well trained chemists in chemical works is now becoming much more general than heretofore, especially on the continent, where in some cases a considerable staff is employed and provided with suitable appliances, for the purpose not only of attending to and perfecting the ordinary operations which are in use, but in making investigations in relation to the class of manufacture they are engaged in. A conviction of the necessity of this is gaining strength in this country, though not so quickly as might be desired; nevertheless these things are encouraging.”

Before proceeding with the subject it must be remarked that the learned president recounts the triumphs of organic chemistry in connection with the coal-tar colours really as a plea for an encouragement of research, this will explain the tone and tendency of his language.

“It was in 1856, now twenty years since, that this industry was commenced by the discovery of the ‘mauve’ or ‘aniline purple.’ It may be of interest to state that it was in Scotland, in the autumn of the same year that the first experiments upon the application of this dye to the arts of dyeing and calico printing were made, at Perth and Maryhill.

I need scarcely remind you of the wonderful development of this industry since then, seeing we now have from the same source colouring matters capable of producing not only all the colours of the rainbow, but their combinations. I wish, however, to briefly refer to the date and origin of the products which have served to build up this great industry.

It was in 1825 that Faraday published, in the *Philosophical Transactions*, his research on the oily products separated in com-

pressing oil-gas, and described a substance he obtained from it—a volatile colourless oil, which he called Bicarburetted Hydrogen. Mitscherlich some years afterwards obtained the same substance from benzoic acid and gave it the name it bears, viz., 'Benzol.' This same chemist further obtained from benzol, nitro-benzol, by acting upon it with nitric acid. Zinin afterwards studied the action of reducing agents upon nitro-benzol, and obtained 'aniline,' which he at that time called Benzidam.

Again, Pelletier and Walter discovered the hydrocarbon toluol in 1837. Deville produced its nitro-compound in 1841; and Hofmann and Muspratt obtained from this 'toluidine,' by the process used by Zinin to reduce nitro-benzol.

I might mention other names in connection with these substances, such as Runge and Unverdorben; but I would now ask, Did any of these chemists make these investigations with the hope of gain? was it not rather from the love of research, and that alone? and now these products, which were then practically useless, are the basis of the aniline colours. But to go further: Doebereiner a long while ago obtained from alcohol a substance which he called 'light oxygen ether,' now known as aldehyd. Gay-Lussac produced iodide of ethyl in 1815. Dumas and Peligot discovered the corresponding substance iodide of methyl in 1835; but, as in the cases I have previously referred to, these bodies had no practical value, and were never prepared but in the laboratory. Hofmann, in his researches on the molecular constitution of the volatile organic bases, discovered in 1850 the replacement compounds of aniline containing alcohol radicals.

All these compounds have now been manufactured on the large scale, and used in the further development of the industry of these artificial colouring matters.

Other substances might be mentioned; but I think these are sufficient to show how the products of research which, when first discovered and for a long period afterwards, were only of scientific interest, at last became of great practical value; and it is evident that, had not the investigations and discoveries I have referred to been made as they were solely from a love of science, no aniline colours would now be known.

The colouring-matters I have hitherto spoken of are nitrogenous, and derived from benzol and its homologues. There are a few others, however, of the same origin which contain no nitrogen ; but they are of secondary importance.

I now pass on to another class of colouring-matter, which is obtained from anthracen, a coal-tar product differing from benzol and toluol in physical characters, inasmuch as it is a magnificent crystalline solid.

The first colouring-matter derived from anthracen which I wish to draw your attention to, is alizarin, the principal dyeing agent found in madder-root. This substance was for a long time supposed to be related to naphthalin, inasmuch as phthalic acid can be produced from both of them ; and many were the experiments made by chemists in this direction ; it was not, however, until 1868 that this was proved to be a mistake, and its relationship to anthracen was discovered by Graebe and Liebermann, who succeeded in preparing this coal-tar product from the natural alizarin itself.

Having obtained this important result, they turned their attention further to the subject, hoping to find some process by which alizarin could be produced from anthracen ; in this they were soon successful.

The discovery of the artificial formation of alizarin was of great interest, inasmuch as it was another of those instances which have of late years become so numerous, namely, the formation of a vegetable product artificially ; but the process used by Graebe and Liebermann was of little practical value, because too expensive for practical purposes.

Having previously worked on anthracen derivatives, it occurred to me to make some experiments on this subject, which resulted in the discovery of a process by which the colouring matter could be economically produced on a large scale. Messrs. Caro, Graebe, and Liebermann about the same time obtained similar results in Germany ; this was in 1869. Further investigation during that year yielded me a new process, by which 'dichloranthracen' could be used in place of the more costly product anthraquinon, which was required by the original processes. I mention this, as most of the artificial alizarin used in this country up to the end of 1873, and a good deal since, has been prepared by this new process.

It was observed that when commercial artificial alizarin prepared from anthraquinon, but more especially from dichloranthracen, was used for dyeing, the colours produced differed from those dyed with madder or pure alizarin ; and many persons therefore concluded that the artificial colouring matter was not alizarin at all. This question, however, was set at rest by separating out the pure artificial alizarin from the commercial product and comparing it with the natural alizarin, when it was found to produce exactly the same colours on mordanted fabrics, to have the same composition, to give the same reactions with reagents, and to yield the same products on oxidation.

But whilst examining into this subject it was found that a second colouring-matter was present in the commercial product, and in somewhat large quantities, especially when dichloranthracen had been employed in its preparation ; and to this was due the difference in shade of colour referred to.

This substance, when investigated, was found to have the same composition as 'purpurin,' also a colouring-matter found in madder, but of very little value on account of the looseness and dulness of some of the colours it produces. This new substance being derived from anthracen, was named anthrapurpurin ; unlike its isomer purpurin, however, it is of great value as a colouring-matter. I do not think I shall be going beyond the results of experience if I say it is of as great importance as alizarin itself ; with alumina mordants it produces reds of a more scarlet or fiery red than those from alizarin. In fact, so fine are the colours produced that, with ordinary alumina mordants on uniled cotton, it gives results nearly equal in brilliancy to Turkey-red produced with madder or garancin ; and I believe the rapid success of artificial alizarin was greatly due to its presence. Most of that consumed at first was for Turkey-red dyeing ; and the colours were so clear that it was mostly used in combination with madder or garancin, to brighten up the colours produced by these natural products.

The purple colours anthrapurpurin produces with iron mordants are bluer in shade than those of alizarin, and the blacks are very intense. Its application is practically the same as alizarin, so that they can be used in combination.

As already noticed, the commercial product called 'artificial

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alizarin' first supplied to the consumer was always a mixture of alizarin and anthrapurpurin; and various mixtures of these two colouring-matters are still sent into the market; but, owing to the investigations that have been made and the study and attention that has been given to it by manufacturers, nearly pure alizarin and anthrapurpurin are also sent into the market—the first being known as 'blue-shade alizarin,' and the second as red or 'scarlet alizarin.'"

Mr. Perkin then goes at length into the reasons why different methods of preparing artificial alizarin yield products containing more or less anthrapurpurin; the illustrations are purely chemical and we omit them.

"At first it was supposed by many that the quantity of coal-tar produced would not yield a sufficient supply of anthracen for the manufacture of artificial alizarin. Experience has, however, proved that this supposition was groundless, as now the supply is greater than the demand.

Moreover, some very interesting experiments have lately been made, by which anthraquinon and its derivatives have been obtained without the use of anthracen. The most interesting are those in which phthalic anhydride is employed with benzolic derivatives; for example, this anhydride gives with hydroquinon a colouring matter having the same composition, as well as most of the other properties of alizarin. It is called quinizarin. Baeyer and Caro have also obtained from phthalic anhydride and phenol oxyanthraquinon, and by using pyrocatechin in place of phenol they got alizarin itself.

Although these products have not been obtained in sufficient quantities by these processes to be of any practical value, we do not know what further research may do. Already one of the substances used is being prepared on the large scale for the manufacture of that beautiful colouring matter 'eosin,' I refer to phthalic anhydride.

Now, with reference to the origin of the products which are used for the manufacture of artificial alizarin, we find the first researches made in reference to anthracen were by Dumas and Laurent in 1832; subsequently, Laurent further worked upon this subject, and obtained, by the oxidation of this hydrocarbon, a substance which he called anthracenuse; he also obtained dichloranthracen. Dr.

Anderson also made an investigation on anthracen and its compounds in 1863, and assigned to it its correct formula; he re-examined its oxidation product, which Laurent called anthracenuse, and named it oxyanthracen, the substance we now know as anthraquinon.

All these substances were without any practical value until 1868; but we now find them of the greatest importance, and used daily in immense quantities.

But to bring out more clearly the practical importance of these fruits of scientific research, it will be well perhaps to see what has been their influence on the colouring matters which were in use before them, and also the extent of their present consumption.

The influence of the so-called aniline colours on dye-woods, &c., has been remarkably small. It is true that at first magenta had a depreciating influence upon cochineal; but this has passed away, and now the consumption of that dye is as great as ever; certainly its price is much lower than it used to be, but this is due to a variety of causes, especially the great increase in the cultivation of the insect at Teneriffe. And perhaps this want of influence is not so very remarkable when we consider the aniline colours are entirely new products, differing in composition and properties from the old colouring matters, and therefore could only displace them to a certain extent.

But whilst this is the case, the aniline colours have been more and more used, until at present it is computed that their annual sale in the United Kingdom and on the Continent exceeds £2,000,000. This is probably due to new applications and increase of trade.

When, however, we come to consider the influence of the anthracen colours, alizarin and anthrapurpurin, more generally known as 'artificial alizarin,' we find we have a very different tale to tell.

Here, in the case of alizarin, we have a competition not between two colouring matters, but the same from different sources—the old source being the madder-root, the new one coal-tar. And when we introduce the consideration of anthrapurpurin, which produces such magnificent reds, much brighter than alizarin or ordinary purpurin, we see we have not only a replacement but an improvement, so that these new colouring matters throw the old ones into the shade. The

products being purer, the clearing processes for goods dyed with them are also necessarily easier and simpler.

It will be interesting to examine into the statistics of the madder and garancin trade in a brief manner, to see what has been the influence of artificial alizarin on their consumption. The following figures are mostly calculated from the Board of Trade returns.

During the ten years immediately preceding the introduction of artificial alizarin the average annual imports of madder into the United Kingdom were 15,292 tons, and of garancin 2278 tons. Estimating the value of the former at £2 2s. 6d., and the latter at £8 per cwt., which were about the average prices during that period, the annual value in round numbers was about one million sterling.

The introduction of artificial alizarin, however, has so influenced the value of madder that its price is now less than one-half; and thus a saving of over half a million sterling per annum has been effected to the manufacturers of the United Kingdom, one-half of which may be put down to Glasgow.

So much for its effect in reducing prices; but what has been its influence on the consumption of these dye-stuffs?

I have already stated the average quantity of these substances imported per annum prior to the discovery of the artificial product, and will now compare it with the imports of last year and this. That for the present year of course is an estimated quantity, and calculated from the returns for the first seven months.

		Average Annual Imports.		
		1859-1868.	1875.	1876.
		Tons.	Tons.	Tons.
Madder		15,292	5014	3653
Garancin		2278	1293	813

These figures speak for themselves.

The money value, which was formerly £1,000,000 per annum, is now, calculating from the estimated quantity for the year, only £138,105, say £140,000, taking garancin at £4 per cwt. and madder at £1 per cwt., prices slightly in excess of their present value.

At the present prices the cultivation of madder-roots is unremunerative; and it is to be expected that madder-growing will soon be a thing of the past, thousands of acres of land being at the same time

liberated for the growth of those products which we cannot produce artificially, and without which we cannot exist. The quantity of madder grown in all the madder-growing countries of the world prior to 1868, was estimated to be 70,000 tons per annum; and at the present time the artificial colour is manufactured to an extent equivalent to 50,000 tons, or more than two-thirds of the quantity grown when its cultivation had reached its highest point.

I might have referred to other subjects besides the coal-tar colours which have resulted from scientific research; but I know of no other of such interest and magnitude. From the brief history I have given, we see that the origin of these colouring-matters is entirely the fruit of many researches made quite independently by different chemists, who worked at them without any knowledge of their future importance; and on looking at the researches which have thus culminated in this industry, it is interesting to notice that many, if not most of them, were conducted for the purpose of elucidating some theoretical point.

3. *Critical and Historical Notes concerning the Production of Adrianople or Turkey Red, and the Theory of this Colour.**

BY THEODORE CHATEAU.

Corresponding Member of the Industrial Societies of Mulhouse and Amiens, etc., etc.

Theory of M. Dumas (1846.)—This eminent chemist in his Treatise upon Chemistry applied to the Arts writes:—"If it is a difficult matter at the present time to give an exact and complete explanation of the Turkey red process, it is not so as far as regards the various separate operations which are carried out.

"The Scouring or Cleansing.—It is evident that if this operation by removing foreign substances from the cotton renders the fixing of the colouring matter less certain it also

*Abstracted and condensed from the "Moniteur Scientifique," vi. (3), p. 965. Continued from Vol. ii., p. 141, *Textile Colourist*.

causes the colour when fixed to be better and brighter; but the natural colour of the cotton can only have a very slight influence upon a full dyed red, while the changes which the cotton undergoes in its fibres, either by scouring or bleaching, appear to be of an unfavourable nature.

"As to the *dunging* or sheep dung bath, it is not proved as Vitalis advances, that this operation is of an indispensable nature, for it is quite certain that it may be omitted without any injury to the beauty of the colour.

"The *oiling* is an important operation, the object of which is to render the cloth more capable of fixing the colouring matter, and we conceive its action to be as follows:—

"Reflecting that on the one hand a certain quantity of alkali is always employed along with the oil, and on the other that the so-called emulsive oil is more easily saponified than other kinds of oil, and that it is besides the kind which gives the best results, some persons have considered that there was formation of an acid soap with which all parts of the tissue became impregnated, and which determined the combination of the colouring matter.

"But the exact experiments made by M. Chevreul upon the oily matter extracted from prepared cotton previous to dyeing by means of alcohol shewed that there were no free fatty acids in it. We consider that the action of the alkali is to make an emulsion of the oil and divide it so that it may more readily find an entrance into all parts of the cotton, and consequently produce a more even and solid colour. It is possible to imagine, in fact, that if the cotton is penetrated by an oily fluid, this being displaced under the influence of the dye liquors becomes the cause of some phenomena of endosmose, by means of which, it is known, there can be effected penetrations of matter which are impossible by any other method.

"As to the drying in stoves which follows each oiling operation, its end is evidently to increase the fluidity of the oil and cause it to penetrate more into the interior of the cotton, as it loses the water which filled the pores and becomes in consequence more ready to imbibe oil itself.

"The operation of the alkaline baths consists in removing

the excess of oil which remains in the interstices of the stuff, and which would do more harm than good in the subsequent operations.

"The galling and aluming, which are performed either separately or together, have clearly the effect of giving a darker red, a fact which is matter of daily experience and which could be easily known.

"In the dyeing the red colouring matter is fixed by the special power of the alumina derived from the decomposition of the alum, whether it be present in the state of sub-salt or whether it has undergone a more complete decomposition.

"In the soaping or brightening, where a boiling solution of soap mixed with some alkali is used, any alum which may remain upon the cloth is thoroughly decomposed; on the other hand some brownish substances are probably removed, due either to the madder or to the galls, which, if remaining, would injure the beauty of the colour. M. Chevreul is also of opinion that the alkali may have a modifying influence upon the colouring matter, and give it a more agreeable hue.

"As to the final operation of brightening, in which solutions of tin are employed, it is very difficult to give any rational account of what parts are played by the various materials in use.

"The comparative experiments made by M. Chevreul with cotton dyed red by the ordinary process, and with cotton dyed by the Turkey red process, shew that while the latter is faster than the former to soaping, the contrary is the case when both kinds are exposed together to the action of solar light. Turkey red also loses its colour more easily by friction, which seems to indicate that the colour is rather interposed than profoundly fixed and that in this respect there is some slight difference between it and the common red."

Theory of M. Persoz, Senr. (1846.)—In his celebrated work upon calico printing, M. Persoz gives the following theoretical considerations upon the Turkey red process:—"In oiling the cotton," he says, "it is not sufficient to cover it with a fatty

body, since we know by experience that a drop of oil or a stain of grease in its unmodified state resists the entrance of colour in the part covered, and prevents mordants of iron and alumina from fixing; the nature of the fatty matter must undergo a modification by the assistance of alkalies, or alkaline compounds, under the triple influence of water, heat, and air.

"It is not, however, a simple saponification which takes place under these circumstances, as is stated in some works, for if that was the case it would be sufficient to take an olive oil soap and impregnate the cotton with it, and then set the fatty acids at liberty, to obtain cotton which would take a pink colour when dyed in madder; but this does not happen, and, moreover, the oiling process never succeeds so well as when carbonate and especially the bicarbonates of potash or soda are employed, the saponifying powers of which at ordinary temperatures are incomparably lower than that of the caustic alkalies; the cause must, therefore, be sought in another direction.

"Oil and the alkaline bicarbonates are undoubtedly the principal materials in this operation; but the oil must be of an emulsive quality, and beyond that other substances of a peculiar nature are conjoined, such as sheep or cow dung, which it has been found impossible to do without.

"During the drying after oiling the fatty matter undergoes a change which makes it insoluble in weak alkalies, and it acquires in a high degree the property of strongly adhering to the cloth; but as this change takes place from the surface to the centre, and as the superficial parts of each layer are easily detached, not being in combination with the fibre, it is necessary to repeat the oilings until the centre of the cloth is sufficiently oiled.

"Solar light and heat exercise a great influence upon pieces exposed to the air; in autumn, winter, and spring, there is much more difficulty in fixing and modifying the fatty matter than there is in the summer.

"When the pieces are dried in stoves the effects of the artificial heat are not less observable, and if the right tempera-

ture is not kept up there will be found considerable differences in the depth of the colour.

“What is the change which takes place in the fatty matter when it is exposed on the tissue to the triple influences of air, heat, and alkaline carbonates? What are the products into which it is metamorphosed? In short, what is the formula which explains this mysterious operation?”

Experiments of M. Weissgerber.—After asking the above questions, M. Persoz details the results of some experiments made in his laboratory in 1839 by one of his pupils, M. Weissgerber.

“This pupil,” he says, “being intended at this time to make Turkey red his speciality, observed that the cloth which was oiled in the regular manner gave up its fatty matter not only to turpentine, but that it could also be completely freed from it by acetone (wood spirit); he cut up some oiled cloth into small portions, and by means of a displacement apparatus he succeeded in removing all the organic mordant in solution in acetone. He assured himself of this as follows: Whenever he passed the oiled cloth in a madder bath it dyed up a medium red, which, by soaping and other treatments, yielded a good, full pink; but when this same cloth was treated with acetone it gradually lost its power of attracting colouring matter, until when the action was complete it no longer became coloured in the dye bath. The acetone used to dissolve the mordant was distilled off in a water bath and there was left a residue in the retort of a thick liquid of a fatty nature, which separated into a solid and a liquid layer, and remained in that condition for a long time.

“With the intention of ascertaining if this thick liquid still possessed the properties of the oil from which it had been produced, he saponified it by strong bases, but not succeeding in finding any glycerine in the products of the saponification, he was obliged to conclude that the substance had disappeared.

“Lastly, it was proved and verified by several experiments, that by applying a proper quantity of this modified fatty matter to cloth, and dyeing in madder, the darkest and purest shades could be obtained.

M. Persoz adds, "after what we have seen we are convinced that if ever this fatty substance can be directly prepared there will no longer be any necessity to use mordants of alumina." He continues, "this statement, which at first sight seems so extraordinary, is supported by an observation made by M. Chevreul, about 1839, upon a certain Turkey red which he analyzed, and from which he could only extract a very small quantity of alumina, a substance which is used pretty largely in Turkey red dyeing. If the glycerine disappears in this operation it is by submitting to an oxidation and a change which have their causes—the first in the presence of the air and the conditions of temperature in which the oiling is carried out, and secondly, in the use of indispensable nitrogenized matters to put the organic matter in movement. It is without doubt for these substances that there exists the necessity in great measure of having recourse to foecal and excrementious matters. We say in great measure, because from our experiments upon these kind of substances we know that they contain fatty matters in precisely the same state in which it was found upon the cloth, possessing the property of attracting colouring matters. This leads us to ask if it would not be possible to make use of the act of digestion in certain animals to change these fatty matters and to render them fit to be used under the form of excrements in the process of Turkey red dyeing.

"All those who are practically occupied in Turkey red dyeing know that the oil baths are the more active in proportion as they contain a less or greater proportion of old oil baths which contain a quantity of the modified fatty matters.

"A supposed property of sheep dung is that it prevents the goods heating or firing when they are not properly attended to, which is not an uncommon occurrence. The heating is probably correctly attributed to the absorption of oxygen; now, if the sheep dung has the effect, which there is reason to suppose it has, of rendering the fatty matter more stable by changing it, this would explain the influence which it exercises. The influence which the phosphates contained in the excrementious matters may have in the operations which

succeed the oiling should probably also be taken into account."

Thus, according to M. Persoz, the stability of the Turkey red is chiefly due to the formation upon the tissue of a changed or modified fatty substance, and he attributes this obscure modification to the nitrogenized principles contained in the excrementious matters and to the action of air and solar heat.

We may remark that the opinion which M. Persoz expresses concerning the inutility of alumina is, in our opinion, much too confident and is in opposition to the teachings of practice.

*M. Schützenberger's Theoretical Views (1867).**—"Before mordanting with alumina the cloth or yarn is prepared with a fatty matter (emulsive oil) which is properly modified or changed by the successive actions of alkaline carbonates, heat, light, and atmospheric influences.

"The product into which the emulsive oil is changed acts itself as a mordant, and attracts colour from the madder dye so as to give a medium red, which by soaping and brightening becomes a good pink. When combined with alumina or oxide of iron it communicates remarkable stability to the coloured lake produced, which allows of vigorous cleansing and brightening.

The key to the dyeing of Turkey red, according to M. Schützenberger, is "*in the action of the fatty matter and the quite special change which it is made to undergo.*"

He adds, "we are still ignorant of the precise nature of the change of the fatty matter, or by what kind of transformation it becomes able to fulfil so useful a part. Is it possible to accomplish this change independent of the cloth so that the fat could be applied directly by a simple padding or printing? This question, which is of great importance, has up to the present time vainly exercised the abilities of the best chemists.

After describing in brief the preparation of the oil baths M. Schützenberger adds:

"The experiments of M. Ed. Schwartz (also quoted by Persoz) shew the necessity of the intervention of alkalies and

* *Traité des Matières Colorantes*, ii., p. 280.

by preference the alkaline carbonates or bicarbonates. According to the results obtained by this able technological chemist, the alkalies do not act merely as agents in promoting the emulsion or fine division of the fatty matter, but they have another important influence in the progress of the change which takes place.

"It seems also that it is useful to add to the oily liquors a certain proportion of sheep dung, or cow dung. This addition, made with the intention of what is called animalizing the tissue and making it somewhat similar to a fabric made from animal fibres, may be of advantage, because the constituents of the excrements of herbivorous animals assist in the alteration of the fatty matters.

"Leaving the practical knowledge of this matter, which is entirely defective, we may hypothetically consider the mysterious transformation of the fatty substances to be due to a slow oxidation. This idea is supported to a certain extent by the known phenomena of the absorption of oxygen by fats, and by the spontaneous combustion which sometimes take place in oiled cloth when it is heaped up without precaution or sufficient airing to prevent undue elevation of temperature.

"It is true," he adds, "that experimenters have tried various manners of oxidizing the oil, independent of the tissue, without succeeding in modifying it in any useful manner for the Turkey red process; but this negative result is not an argument against the theory of oxidation, which, if it cannot be distinctly proved, is to say the least, highly probable."

After describing the experiments of M. Weissgerber, given before, M. Schützenberger cites his own trials.

"I have myself," he says, "extracted by means of acidulated alcohol, the fatty matter from a finished Turkey cloth. After saturating the sulphuric acid with ammonia, the solution was concentrated and precipitated by water. The deposit filtered, washed, and dried, was exhausted with sulphuret of carbon, which dissolves the fatty matter with a little of the colour. What is undissolved is pure alizarine. After elimination of the sulphuret of carbon, I obtained an oily residue

of a reddish colour. Treated by baryta water this liquid furnished immediately in the cold a soap of baryta. It therefore contains free fatty acid. The portion not acted upon in the cold was boiled with hydrate of baryta, a further saponification took place, and a fresh quantity of soap obtained; finally there remained a considerable proportion of a non-saponifiable neutral fat, which is probably the matter isolated by M. Weissgerber. The baryta soap thus obtained is soluble in alcohol, from which it crystallizes in needles.

"It is known that the sulpho-oleic acid, obtained by the sulphuric saponification of oil, when decomposed by water, furnishes a substance possessing in a certain degree the power of fastening many madder colours when it is used with the mordant in printing. From this it is probable that it is the oleine of the oil which chiefly contributes to the production of this peculiar organic mordant."*

M. Schützenberger continues: "The modified oil acts:

(1) As a mordant: according to M. Chevreul certain Turkey reds contain only a minimum amount of alumina.

(2) As giving stability to the red lake.

(3) M. Kuhlman has further demonstrated that it possesses in a high degree the property of retaining metallic oxides, such as the oxide of iron.

He adds, "upon consideration we are induced to attribute the peculiar hue and brilliancy of Turkey red to a physical effect. The fluid modified fatty matter with which the tissue is impregnated tends to accumulate upon the surface by capillary action, and, as a consequence, the complex lake is entirely superficial."

M. Schützenberger quotes the observation of M. Persoz that the finest red cloth when cut shows the interior parts to be nearly white.

"The increased stability can also be explained by a physical action of the oil which, enveloping the particles of the lake,

* M. Chateau adds in a foot note: It is curious to see that neither M. Weissgerber, nor M. Persoz, nor M. Schützenberger ever thought of examining from this point of view the various fatty matters which spirits of turpentine, acetone, or acidulated alcohol extract from oiled cloth.

preserves them from the too direct action of natural destroying agents.

"But it may be asked, how is it possible to imagine the dyeing to be accomplished if the mordant cannot be wetted, surrounded as it is by a fluid oil? This objection can be easily removed. The fat easily dissolves the colouring matter and so transmits it to the metallic oxide as readily as water would.

"These considerations are not intended as a denial of all chemical action of the modified oil in the production of the special character of the Turkey red.

"The steeping, after oiling, is with the object of removing the unchanged fatty matter and that portion of the modified oil which does not adhere to the fibre.

"The soaping cannot have the effect of fixing fatty acid upon the fibre; it is, however, possible that the free fatty acid which I found in the oily matter obtained from finished Turkey red was derived from this source. The principal action of the soap, as also of the alkali used with it, is to remove the brown matters and other substances from the alizarine. As to the tin salts employed, they cause without doubt the precipitation of a portion of oxide of tin, which turns the shade of the compound lake and gives it that fiery hue which is one of the characteristics of the Turkey red colour."

[To be continued.]

4. Latest Improvements in Applied Chemistry.

UNDER the title of *Les Derniers Progrès de l'Industrie Chimique* there have appeared for some months past in the scientific serials (we make use of the *Moniteur Scientifique*) extracts from a report edited by the celebrated chemist A. W. Hofmann. The various subjects are entrusted to different hands, who are

presumably *au fait* in their several departments. We have not previously to this month seen anything of special interest to our readers, but in the continuation of the report upon aluminum and its compounds, which is written by M. Rud. Biedemann, of Berlin, the subject of mordants of alumina comes under consideration, and we may accept the report as representing what is believed on the continent to be the latest state of knowledge upon these matters. As there is much in it of interest to the dyer and printer which has not appeared previously in English in a connected form, we believe it will be useful to translate those parts of the report more immediately bearing upon the use of alumina as a mordant.

The author says that "in printing and dyeing preference is commonly given to a neutral alum, which is made by boiling together 12 parts of ordinary alum and 1 part of lime, the use of this neutral alum is to prevent the alteration of colours by an acid reaction." The process and the reasoning are both new to us and we doubt their accuracy. The writer continues: "The active principle of alum resides in the sulphate of alumina, for the sulphate of potash or of soda can be replaced by sulphate of ammonia without the least change in the action of the alum. It would therefore appear rational to employ simple sulphate of alumina. This salt is a commercial article known as concentrated alum (in England called patent alum, *Ed.*); it forms a white slightly translucent mass which can be cut with a knife. But the extension of its application has met with difficulties; it is too easily soluble in water (1 part dissolves in 12 parts of cold water), it crystallizes with difficulty, which prevents it being obtained free from iron. For this reason it is necessary in all those cases where iron is injurious to combine the sulphate of alumina with sulphate of potash, although the latter salt is both costly and inactive, to render the crystallization easy, and its purification more complete." Sulphate of alumina is much more soluble in cold water than is here stated, and on the continent we never had any difficulty in obtaining this salt perfectly free from iron, though it is not readily met with pure in England, the pure sulphate of alumina, quite white and much more opaque than

the English kind, was said to be manufactured in Sweden, but of its origin we know nothing precise. M. Biedermann continues: "The most important application of alum is in dyeing and printing, where it serves as a mordant, an application depending upon the double affinity which alumina possesses for textile fibres and colouring matters.

The action of alum upon woollen fibre has been studied by M. Paul Havrez, who has published his researches.

He has found that relatively small proportions of alum act by depositing hydrate of alumina in the interior of the wool, but if the alum be employed in large quantities the deposited alumina is redissolved, so that wool treated with a large quantity of alum does not dye up colours so dark and bright as when the alum is employed in small proportions; and, further, that it acts best when the solution is hot and the contact with the wool prolonged for a considerable time.

M. Havrez believes that this is explained by the presence of lime in ordinary water. As it might be supposed that the difference of the action of alum, according as it was employed in large or small quantities, was produced by a small quantity of alkali which the wool had retained from the scouring processes, or that ammonia might exist in the wool itself, he washed some wool with water slightly acidified with nitric acid, but this did not interfere with the decomposition of the alum and the deposition of alumina in the interior of the fibre. It is therefore concluded that the wool is itself the active agent.

M. Reimann believes that there is disassociation of the elements of the alum; basic sulphate of alumina being separated while the sulphuric acid, also separated, is diluted with so great a quantity of water as to be unable to exercise any solvent action upon the basic salt deposited upon the fibre. This salt by long contact with water parts with a further portion of its sulphuric acid, leaving a hydrate of alumina containing only a very small portion of acid. But if there is much alum in solution there is difficulty in the formation of the basic salt, which would be redissolved continually by the acidity of the bath.

However this may be, the practical operations are agreeable to the experiments of M. Havrez. All wool dyers know that mordanting with alum is only good to a certain extent; in general the practice is in aluming to take 1 part of alum for 10 parts of wool; to alum 30 lb. of wool, it is necessary to use 3 lb. of alum and 1,500 lb. or 150 gallons of water, or so that the solution contains $\frac{1}{10}$ per cent. of alum.*

If sulphate of alumina be used instead of alum it ought to be not only free from iron, which is the case in good qualities of this salt, but also free from an excess of sulphuric acid. To discover free acid ordinary reagents are useless, because sulphate of alumina itself has an acid reaction. M. Giseke recommends the two following methods: Triturate 5 grammes of the solid sulphate of alumina with 50 cubic centimetres of absolute alcohol, throw the mixture on a filter and wash with absolute alcohol to the bulk of 100 c.c. Sulphate of alumina is insoluble in absolute alcohol, but the sulphuric acid dissolves in it and is all found in the filtrate, where the quantity can be determined by means of a standard solution of soda. But this method is not perfectly accurate, as neutral sulphate of alumina is not altogether insoluble in absolute alcohol. The following process is better:—

If to a very dilute solution of sulphate of alumina or of alum a few drops of tincture of logwood be added, they will produce a characteristic dark reddish-purple when the salt is neutral, and if the salt is acid, only a weak yellowish-brown colour. By this method the presence of 0.2 of free acid in 100 parts can be detected with certainty. To be able to recognize the shade with exactness, it should be compared with a standard liquor which contains in each 100 centimetres 10 c.c. of potash alum, free from acid, and 0.5 c.c. of a tincture of logwood, made by boiling 1 part of wood with 1 part of water, and adding $\frac{1}{10}$ part of alcohol.

* It will be observed that the proportion of alum to the water given above is as 1 to 500, or $\frac{2}{100}$ per cent.; we have never seen the original report by M. Hofmann, and we do not know at present how this mistake arises; besides this, there are many inaccuracies of statement which may either be the fault of the French translator or exist in the original.—*Ed.*

To ascertain the amount of free acid, a solution of 10 grammes of the sulphate is made into 100 c.c. volume, and 0.5 c.c. of the logwood tincture added, then standard solution of soda poured in until the dark violet-red colour is produced.

M. W. Stein uses ultramarine to shew the presence of free acid in sulphate of alumina. Unsized paper, coloured lightly with ultramarine, is bleached by sulphuric acid.

Alumina is advantageously employed in dyeing and printing, under the form of aluminate of soda. In 1819, Macquer and Hausmann advised the use of aluminate of potash in dyeing. With this mordant the colours differ more or less from those produced with alum, depending upon the nature of the colouring matter. To obtain the same shades as from alum, the aluminate of soda should be transformed into an acid mordant.

M. R. Wagner has remarked that the best alumina mordant is obtained from ethylamine aluminate. Ethylamine easily dissolves alumina, and when the solution is exposed to the air the ethylamine evaporates and leaves the alumina pure. It is possible that sooner or later ethylamine may be manufactured on the large scale at a sufficiently low price to be used in practice.

Aluminate of soda owes its activity to its easy decomposition, which is effected even by carbonic acid; alumina separates, which forms lakes with the colouring matters.

M. P. Morin, who was one of the first to employ aluminate of soda in the production of lakes, mixes the colouring matter with the aluminate, and precipitates by sulphuric acid. The hue of the lakes shows a difference, according as the addition of acid is regulated to leave the liquid acid, alkaline, or neutral.

An inconvenience in the preparation of lakes is that they do not readily subside, whether made hot or cold, or however the mixture is accomplished. The difficulty is in some measure overcome by causing the lake to be formed in one litre of water, supposing it takes three litres to wash it. When the lake is produced it is well agitated, and then the two litres of water are added and again stirred up; the lake

then settles, and occupies only one-third of the volume of the liquid.

M. Dullo has communicated a process of preparing alumina in a state very suitable for the preparation of lakes. The alumina, precipitated by ammonia, is in a gelatinous form, which contracts excessively upon drying, forming fissures. The alumina, precipitated from aluminate of soda by carbonic acid, at a temperature of 122° F., is in the form of a compact powder. Precipitated at higher temperatures, the powder is still more and more dense, until it becomes too much so for dyeing and printing purposes. If the precipitation is conducted at a low temperature, the alumina takes the gelatinous form the same as when precipitated by ammonia. It is produced in the same state when alum is boiled with metallic zinc; it is then extremely pure.

By altering the process in the following manner, the alumina is obtained in the form of a very fine powder, not at all gelatinous, depositing well in a grain of extreme tenuity: Dissolve 1 lb. of alum in $\frac{1}{2}$ gallon of water, and add 75 grains of sulphate of copper and about $\frac{1}{4}$ lb. of zinc turnings, leave the mixture for three days in a warm place, renewing the water lost by evaporation. The copper is first deposited upon the zinc, the two metals thus forming a voltaic couple sufficiently strong; hydrogen is disengaged, sulphate of zinc is formed, and the alumina gradually separates in the state of a very fine powder; the reaction is allowed to continue until there is no more alumina left in solution, or until ammonia ceases to give a precipitate. If the reaction is prolonged beyond this point, oxide of iron will precipitate if present. The alumina washes easily, and does not contract upon drying.

Acetate of alumina is a very useful composition in dyeing. Before the development of the cryolite and bauxite industries it was prepared by decomposing sulphate with the acetates of lead, baryta or soda; but since that time it is found more advantageous to dissolve the alumina precipitated from aluminate of soda in acetic acid. The alumina precipitated by means of hydrochloric acid dissolves more easily in acetic

acid than when carbonic acid is used to precipitate it ; in this last case the solubility of the alumina appears to be considerably impeded by the presence of notable quantities of carbonate of soda. According to M. R. Wagner, this inconvenience is overcome by digesting the alumina for several days either in solution of acetate of alumina containing free acetic acid, or in a solution of chloride of aluminum.

Mr. S. M. Lyte prepares acetate of alumina by dissolving phosphate of alumina in phosphoric acid, and precipitating by acetate of lead, the acetate of alumina remains in solution, and the phosphate of lead which precipitates is used for making phosphorous and phosphoric acid.

M. H. C. Hahn has described a process for directly preparing a mordant of alumina free from iron by means of cryolite. One hundred parts of cryolite washed, and in small pieces, are mixed with 88 parts of milk of lime ; the mixtures heated by steam in a wooden vat made without iron nails ; upon boiling the decomposition is complete. When the fluoride of calcium has deposited, the clear liquid is drawn off and diluted to 10° B. It is exactly neutralized with commercial acetic acid at 6° B. ; after a sufficient time two-thirds of the bulk can be drawn off clear, and furnishes pure acetate of soda. The remaining portion is mixed with one-third of the amount of acetic acid first used, and then with 46 parts of sulphuric acid at sp. gr., 1.83 ; a solution is by this means obtained containing a mixture of sulphate of soda and an aceto-sulphate of alumina, which is perfectly free from iron.

5. *A New Reducing Agent for Indigo Dyeing.**

PROFESSOR Clouet, of the Medical School at Rouen, has made a study of a substance sent by the French Government to the Industrial Society of that town for examination as to

* See Bull. de la Soc. Ind. de Rouen, iv., p. 344.

its value as an agent on dyeing. This substance consists of the grains of a plant (*Cassia tora* of Linnæus) growing in the East Indies, Arabia, Japan, and Cochin China, and known under the name of Tagarey-verey in Pondicherry and other parts of Hindostan. In the East it is regularly used as a component of the indigo vat, and serves the same purpose as the bran, madder, or molasses used in Europe, with this difference, that here artificial heat is employed to promote the action of the reducing agents, while on the Coromandel coast the natural heat alone is employed. The so-called hot-vats are chiefly used among us for wool dyeing, but in India cotton is the material for which they are employed.

The analysis of these grains shewed the presence of tannic acid, chrysophanic acid, sugar, gum, and starch, but nothing was learned from it which gave a clue to its special properties as a reducing agent.

The experiments detailed in the paper were made with a view to ascertain whether these grains could be economically used in France, and whether they presented any advantage over the reducing agents at present in use.

The method of using the Tagarey-verey by the native dyers is given as follows: For dyeing 10 pieces, measuring about 200 yards in length with a width of 25 inches (representing 117 square metres of cloth), there are used about 11¼ lb. of the grains; they are first steeped in 5 or 6 gallons of cold water and then boiled for three or four hours. The grains are swollen and softened by this treatment, the water becomes thick and gummy, and the whole is then added to the indigo vat. In fifteen hours the vat is ready to dye. This operation is repeated every day.

According to information received, the price of the grains in India is about 3 rupees per 100 kilogrammes (say 2 cwt.) The question to be answered was: Would the use of this material be cheaper than the materials at present used for the ordinary copperas vat?

M. Benner kindly communicated the proportions of drugs used in making a copperas and lime vat as at present used; they are as follows:—

44 lb. Java indigo.
 121 lb. sulphate of iron.
 106 lb. quick lime.
 1,870 gallons water.

After one day's work the vat requires freshening up with say 12 lb. of sulphate of iron and 11 lb. of quick lime; it then works for two days and is freshened up with the same quantity of materials; and another time receives the addition of the same drugs before it is considered spent. This represents a consumption of about 157 lb. of sulphate of iron. Now to obtain a shade of blue similar to the so-called Guinea blue, the above materials would dye a quantity of cloth equal to 2,362 square metres, and reckoning the cost of the sulphate of iron at 10 francs the 100 kilogrammes, the cost of the salt per square metre comes out as 0.00302 franc. The 11¼ lb. of Targarey-verey dye 117 square metres at a cost per metre of 0.00364 franc. The results therefore shew against the Indian grain, even when it is reckoned at its selling price in Pondicherry without adding anything for freight. To this there is the disadvantage and cost of having to use heat for the grains. It is therefore concluded that the Tagery-verey cannot be profitably employed in indigo dyeing in Europe.



6. *M. Michel de Vinant on Dyeing, Printing, and Bleaching.**

Crimson by Padding.—Two gallons sapan wood at 13° Tw., 2 gallons thin tragacanth gum water, 2½ lb. double chloride of tin,† 3 oz. nitrate of copper at 84° Tw., the pieces are padded in this mixture, hung up for two days, washed and finished.

* Continued from p. 161.

† We believe this means the bichloride of tin; what is called double muriate of tin in England, means in some localities a concentrated solution of the proto-muriate of tin, in others it means the bichloride.—*Ed.*

Safflower Pink.—For about 110 yards of calico perfectly white, take $\frac{1}{4}$ litre of the prepared safflower extract, at 25 fr. the litre, and mix with amount of water necessary, pass as much cloth as required freshening up at the rate of $\frac{1}{4}$ litre for 110 yards; then in the same bath add 1 litre lime juice at 9° Tw., and freshen up as required; dry at a gentle heat, if possible in the air. This pink-dyed calico must be finished with as little heating as possible. The following paste may be used for finishing :—

3 gallons water.
 $1\frac{3}{4}$ lb. potatoe starch.
 $1\frac{3}{4}$ lb. white starch.
 4 oz. white fat.

Boil, and add $\frac{3}{4}$ pint of lime juice. Use this paste at about 90° F., and dry the goods in the air.

Flesh Colour.—Pass twice through weak annatto liquor, wash, and then dye a safflower pink upon it as in the last receipt.

Apple Green.—For 20 lb. weight of cloth, pass twice in red mordant at 10° Tw., dry, hang for forty-eight hours, wash in running water, dye at 140° F. in quercitron liquor at 1° Tw., or else fustic until the desired shade is obtained; then add 2 lb. of extract of indigo, or sufficient to give the right colour, without washing pass through a solution of 10 gallons water, 2 lb. extract of indigo, and 10 lb. gum substitute, and dry at a gentle heat. Finish with the following :—

4 lb. potato starch.
 5 gallons of water.
 4 lb. white starch.
 1 gallon red liquor at 12° Tw.
 $\frac{1}{2}$ lb. fat.

To which may be added a quantity of the mixed yellow and blue used for the dyeing.

Prussiate Green.—For 30 lb. of cotton cloth; first dye yellow with either weld or quercitron bark, wash and treat for half-an-hour with 3 lb. nitrate of iron at 84°, and 3 oz. crystals of tin at a temperature of 100° F., and afterwards wash.

Then dissolve $1\frac{1}{2}$ lb. yellow prussiate in warm water at 100° F., and add $\frac{3}{4}$ lb. sulphuric acid, work in for half-an-hour and wash. Dye again at 160° F. in bark or weld, with addition of a little alum, lift, and without washing finish off in an extract of indigo liquor, mixed with a little alum.

Chrome Orange.—Dissolve at a boiling heat $12\frac{1}{2}$ lb. of sugar of lead, and $6\frac{1}{4}$ lb. of powdered litharge in $3\frac{1}{2}$ gallons of water, filter, and reduce to 24° Tw. Pass the pieces twice in this liquor, and then in a mixture of lime and water, to which some of the above lead liquor has been added and well mixed, rinse. Dye cold in bichromate of potash acidified with sulphuric acid, and wash. To raise the orange, pass through boiling lime and water. Another method given by M. de Vinant, as used in Manchester, is to raise the orange colour at once without dyeing yellow, in what is called caustic chrome, that is a mixture of bichromate of potash and lime.

Process for Dyeing Royal Blue on Cotton.—Sixty gallons of water at 122° F., 9 lb. nitrate of iron at 84° Tw., $1\frac{1}{2}$ lb. tin crystals. Work in this mixture for half-an-hour, and wash well. Then pass for half-an-hour in 60 gallons of water at 122° , $2\frac{1}{2}$ lb. of yellow prussiate of potash and $1\frac{1}{2}$ lb. of sulphuric acid; then, without washing, pass back into tin and iron bath above, and work in it half-an-hour; wash very well, and give another half-hour in the prussiate bath. Freshen up the first bath with 2 lb. of nitrate of iron and 10 oz. of crystals of tin, pass again half-an-hour in it, wash well, and pass again in the prussiate, freshened up with $\frac{3}{4}$ lb. of prussiate and 1 lb. sulphuric acid, and wash off.

This is the old process of dyeing Prussian blue, the repeated passages in the separate baths are, of course, to increase the depth of colour; the washing out of the tin and iron bath before entering into the prussiate is to avoid loss of prussiate by precipitation of Prussian blue in the bath, or the superficial deposition of it upon the cotton, which would cause the goods to be dusty when dried.

For purposes of reference and comparison, and not as possessing any particular novelty or excellence, we give

receipts for several, chiefly grey and drab, shades upon cotton, from De Vinant, commencing with the various standard liquors employed, and which are afterwards referred to by their numbers.

Catechu Standard No. 1.—5 gallons boiling water, 4 lb. yellow catechu— $1\frac{1}{4}$ lb. sulphate of copper. Use the clear.

Wool Catechu Standard No. 2.—60 gallons boiling water—6 lb. sulphate of copper—20 lb. brown catechu. Boil half-an-hour and use the clear.

No. 3 Standard.—60 gallons hot water— $2\frac{1}{2}$ lb. bichromate of potash.

No. 4 Standard.—10 gallons boiling water— $1\frac{1}{2}$ lb. bichromate of potash—2 lb. sulphate of iron—2 lb. acetic acid.

No. 5 Standard.—50 gallons water—10 oz. sulphate of iron. Let deposit, decant off the clear, and add to it 1 lb. acetic acid.

No. 6 Standard.—10 gallons boiling water—7 lb. sumach. Boil together for fifteen minutes, use the clear.

No. 7 Standard.—10 gallons water—10 lb. bruised galls. Boil two hours and use the clear.

No. 8 Standard.—10 gallons water—10 lb. bablah in powder. Boil two hours and use the clear.

No. 9 Standard.—10 gallons water—10 lb. alder bark. Boil three hours and use the clear.

No. 10 Standard.—10 gallons water—10 lb. chestnut bark. Boil two hours and use the clear.

No. 11 Standard.—10 gallons water—10 lb. divi-divi, broken. Boil three hours and use the clear.

No. 12 Standard.—10 gallons water—10 lb. quercitron bark. Boil two hours and use the clear.

No. 13 Standard.—10 gallons water—5 lb. logwood. Boil two hours and use the clear.

Salmon Colour, No. 1.

1 part No. 2 standard.

8 parts water.

Give two ends, leave on the roll two hours, then pass into No. 3 standard, leave one hour and wash.

Light Brown, No. 2.

6 parts water.

1 part No. 2 standard.

Give two ends, leave on the roll two hours, then pass into No. 3 standard, leave one hour and wash.

Light Chocolate and *Ventre de Biche* are dyed in precisely the same manner and with the same materials by diminishing the proportion of water to the catechu standard.

Olive, No. 5.

1 part No. 2 standard.

6 parts water.

Give two ends; two hours afterwards pass into No. 4 standard, leave one hour and wash off.

Yellow (Jaune Maure), No. 6.

1 part No. 1 standard.

1 part water.

Give two ends; two hours afterwards pass in No. 3 standard, leave one hour and wash.

Common Grey, No. 7.

1 part logwood standard No. 13.

1 part sumach standard No. 6.

4 parts water.

Give two ends, and then pass into No. 5 standard, then wash.

Pearl Grey, No. 8.

1 part No. 10 standard.

5 parts water.

Give two ends, and then pass into No. 5 standard.

Light Grey, No. 9.

1 part No. 9 standard.

5 parts water.

Give two ends, and then pass into No. 5 standard.

Pink Grey, No. 10.

1 part No. 11 standard.

4 parts water.

Give two ends, and then pass into No. 5 standard.

Mouse Grey, No. 11.

1 part No. 7 standard.

3 parts water.

Give two ends, and then pass into No. 5 standard.

Pearl Grey, No. 12.

1 part No. 8 standard.

3 parts water.

Give two ends, and then pass into No. 5 standard.

Olive, No. 13.

1 part No. 12 standard.

2 parts water.

Give two ends, and then pass into No. 5 standard.

Merdois, No. 14.

1 part No. 7 standard.

1 part No. 1 standard.

6 parts water.

Give two ends, and two hours afterwards pass into No. 4 standard.

Light Grey, No. 15.

2 parts No. 7 standard.

5 parts water.

Give two ends, and two hours afterwards pass into No. 5 standard ; wash.

Sumach Grey, No. 16.

2 parts No. 6 standard.

5 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Steel Grey, No. 17.

1 part No. 8 standard.

2 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Slate Grey, No. 18.

2 parts No. 9 standard.

3 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Dark Pearl Grey, No. 19.

1 part No. 10 standard.

2 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Dark Grey, No. 20.

1 part No. 11 standard.

2 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Miller's Grey, No. 21.

1 part No. 6 standard.

1 part No. 13 standard.

4 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Dark Miller's Grey, No. 22.

1 part No. 6 standard.

2 parts No. 13 standard.

2 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash

Dark Pearl Grey, No. 23.

1 part No. 6 standard.

4 parts No. 13 standard.

2 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Bluish Light Grey, No. 24.

1 part No. 6 standard.

6 parts No. 13 standard.

4 parts water.

Give two ends, and one hour afterwards pass into No. 5 standard ; wash.

Pearl Grey, No. 25.

1 part No. 1 standard.

1 part No. 13 standard.

7 parts water.

Give two ends, and one hour afterwards pass into the standard N. No. 1, below, and wash.

Standard N. No. 1.—1 part standard No. 4, 2 parts water.

Steel Grey, No. 26.

1 part No. 2 standard.
1 part No. 13 standard.
7 parts water.

Give two ends, and two hours afterwards pass into the Standard N. No. 1, above, and wash.

Feuille Mort, Dead Leaf, No. 27.

2 parts No. 2 standard.
1 part No. 13 standard.
8 parts water.

Give two ends; and two hours afterwards pass into N. No. 1 standard; wash.

Angora Grey, No. 28.

1 part No. 6 standard.
1 part No. 7 standard.
8 parts water.

Give two ends, and then pass into No. 5 standard; wash.

Light Steel Grey, No. 29.

1 part No. 6 standard.
2 parts No. 7 standard.
7 parts water.

Give two ends, and then pass into No. 5 standard; wash.

Tourterelle, or Pigeon Grey, No. 30.

1 part No. 2 standard.
1 part No. 11 standard.
6 parts water.

Give two ends; two hours afterwards pass into N. No. 1 standard; wash.

Salmon Grey, No. 31.

1 part No. 2 standard.
1 part water.

Give two ends; two hours afterwards pass into N. No. 1 standard; wash.

Olive Grey, No. 32.

2 parts No. 2 standard.

1 part No. 12 standard.

6 parts water.

Give two ends; two hours afterwards pass into N. No. 1 standard; leave two hours and wash.

Light Grey, No. 33.

1 part No. 2 standard.

1 part No. 9 standard.

8 parts water.

Give two ends; two hours afterwards pass into standard N. No. 1; leave two hours and wash.

Ash Grey, No. 34.

1 part No. 2 standard.

3 parts No. 8 standard.

1 part No. 7 standard.

10 parts water.

Give two ends; two hours afterwards pass into standard N. No. 1; leave two hours; wash.

Silver Grey, No. 35.

3 parts No. 2 standard.

2 parts No. 11 standard.

1 part No. 12 standard.

10 parts water.

Give two ends; two hours afterwards pass into standard N. No. 1; leave two hours; wash.

Dark Pigeon Grey, No. 36.

2 parts No. 2 standard.

2 parts No. 11 standard.

2 parts No. 12 standard.

10 parts water.

Give two ends; two hours afterwards pass into No. 11 standard; leave two hours; wash.



7. *Upon a Peculiar Property of Aurantia.*

M. R. GNEHM, of Zurich, in the September number of the *Berichte der Deutschen Chemischen Gesellschaft*, draws attention to a property of the colouring matter called aurantia, which is of some importance to those who have to practically apply it. Aurantia has been for some time manufactured by the Berlin Aniline Colour Company, and it has come into use for dyeing wool and silk of a fine orange colour. Gnehm's attention was drawn by Nölting, of Lyons, and Meister, of Thalweil, to the similarity which this product had to a substance discovered and described by him some time before, and he took the trouble to ascertain the constitution of the colouring matter; he says:—

“The commercial product is in the form of a brick-red powder, soluble in water, from which it can be obtained in reddish brown crystals, and proves to be the ammonia salt of an acid melting and decomposing at 238° , which from all its properties is without doubt identical with the body I described in this Journal (*Berichte* vii., p. 1399), under the name of dipicrylamin (hexanitrodiphenylamin). The colouring constituent of this material is therefore the same as the ammonia salt of hexanitrodiphenylamin, which I likewise described.

“The tinctorial properties of the hexanitrodiphenylamin and its salts, which were long ago known to me, induced me to make experiments for its manufacture on the large scale, in the well-known aniline works of Bindschedler and Busch, of Basle, and towards the end of 1874 the ammonia compound was brought into the market by this firm; but it was soon withdrawn again, and its manufacture entirely given up, on account of its exhibiting an entirely unexpected property, which at the commencement had escaped my observation.

“It will not be uninteresting either for manufacturers or consumers of this newly-appeared article of commerce to be acquainted with a possible property of it, which has not yet

been noted; I therefore give the following extract from a paper of mine which appeared more than a year ago.

“A property which has not yet been mentioned, of both hexanitrodiphenylamin and its salts, is of some interest. These bodies are colouring matters, whether suspended in water or in solution; either in water or alcohol they dye silk and wool of a beautiful orange colour (similar to that from phosphine). This would be of some practical importance, especially considering the cheapness of the material, if it were not for another property which prohibits the general employment of these substances.

“*These bodies have a powerful irritating action on the skin, producing a rash, which is similar to that caused by rubbing in croton oil or tartar-emetic ointment.* This effect, however, is not universal; many persons are so affected by extremely dilute solutions, others on the contrary do not suffer from even concentrated liquors.”

“This action is seen principally upon the workmen who employ the colouring matter. Even the silk dyers, who for the most part work only in very weak solutions, are not free from it; in short, these substances cause so much trouble on a works, that their extended employment must be given up.”

In the same journal and immediately following this article is a reply to it by C. A. Martius, who it will be seen is interested in the manufacture of aurantia and not at all inclined to admit the correctness of the statements or conclusions of the Zurich chemist; he says:—

“The foregoing note of Herr Gnehm relates to an orange-yellow colouring matter known as aurantia, which has for some time past been produced in our manufactory and sold to the trade.

“As to the poisonous action which is said to belong to it, because the dyestuff has proved injurious to *particular* individuals, it seems to me that it should rather be attributed to some impurity or to some other method of manufacturing it, for our colouring matter, notwithstanding the statements of Herr Gnehm, has now for nearly twelve months been regularly

and in large quantities manufactured by us, without any of the operatives or chemists occupied in its making, or any of the dyers who have been almost daily working with it, experiencing the poisonous property ascribed to it by Herr R. Gnehm.

"Researches have been expressly made upon this matter by Herr Salkowski, of the Physiological Institute of this place (Berlin), and by the official expert, Herr O. Zuireck, which have satisfactorily demonstrated the harmlessness of our product, and I have not the slightest hesitation in recommending this colouring matter as a perfectly innocent material for the dyehouse.

"I may, moreover, observe that similar idiosyncracies to that observed by Herr R. Gnehm with regard to dipicrylamin, exist also with reference to other substances, for example, acetic acid, arsenic acid, corallin, bichromate of potash, and with some articles of food, and this without affecting their common use.

"I cannot, therefore, admit that aurantia has any more injurious properties than belong to a whole list of other drugs and dyestuffs, which are, however, daily employed in dyeing without hesitation."

So the matter rests at present between Herren Gnehm and Martius.

8. Upon the "Greening" of Aniline Black.

THOUGH aniline black is one of the fastest colours known to dyers and printers, it has its weak side, and that is its tendency, under certain conditions, to lose its full and deep shade, assuming a greenish hue, which gives a dull and disagreeable aspect, not only to the black itself, but to other colours with which it may be associated in calico printing. The causes of this change have occupied the attention of

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many chemists and practical workers, and conspicuous among them several members of the Industrial Society of Rouen. Messieurs Lamy, Glanzmann, Dépierre, and Witz have separately communicated the results of their experiments and the conclusions they have come to upon this matter. They do not agree in several important details, but as their papers are both able and interesting, and undoubtedly valuable contributions to our knowledge of this remarkable colour, we give here a full translation of them from the first and second volumes of the Bulletin of the above-named Society.

M. F. Lamy's communication is as follows :—

When a weak solution of aniline salt, either the sulphate, tartrate, or muriate is thickened with the addition of oxidizing bodies, printed with roller, and properly oxidized, two very distinct shades of colour are obtained, according to the method of raising or fixing, which may be in one case accomplished by weak or strong solutions of bichromate of potash, and in the other by means of carbonate of soda.

Thus, by passing in bichromate of potash, soaping, and clearing either in weak hypochlorite of soda or common bleaching powder solution, a violet shade is obtained ; by passing in carbonate of soda, soaping, and washing, a bluish shade results.

By steeping specimens of these two shades in muriatic acid at $1\frac{1}{2}$ Tw., and temperature of 60° to 65° F., it will be observed that the violet shade resists the action of the acid better than the blue shade, which immediately changes to green.

Considering the results of this experiment, we asked ourselves whether this blue and violet were not the same body at a different stage of oxidation, and whether the black itself was not composed of a number of layers of these shades also at a certain degree of oxidation. The following experiments seem to give support to this idea :—

If we take bits from a piece printed with aniline black during the time of its oxidation in the ageing room, and submit them to the action of bichromate of potash and carbonate of soda, we shall have as many shades of violet

and blue as we have different times of the ageing. When the aniline black has been completely oxidized, and portions treated on the one hand with bichromate and cleared, and on the other by carbonate of soda, we shall obtain a violet-black in the first case, and a blue-black in the other. The violet-black resists the action of washing, acids, and light much better than the blue-black.

To confirm these results we experimented upon a black containing a large proportion of aniline ($\frac{9}{10}$ lb. of liquid aniline per gallon of colour). After ageing in the room at a temperature of 86° F. dry bulb, and 82° F. wet bulb, for a period of time varying from eighteen to forty-eight hours, a portion of the black was passed in bichromate of potash, washed, and passed into alkaline hypochlorite of soda; a second portion was passed into solution of bleaching powder and washed, and a third into alkaline hypochlorite of soda and washed; a fourth into alkaline hypochlorite and weak carbonate of soda; a fifth into carbonate of soda, washed, soaped, and passed into alkaline hypochlorite; and, lastly, a sixth steamed for three quarters of an hour, chromed and washed. The result of these experiments was that the black which had been most completely oxidized resisted best the attempts to make it green.

We arrived at a point in this direction where a black was obtained scarcely greening at all by light or washing with acid.

Amongst the specimens submitted, there are two upon which particular attention is directed. One made with muriate of aniline, which had forty-eight hours' ageing, and then passed in carbonate of soda and soap; the other made with tartrate of aniline, also with forty-eight hours' ageing, then passed in bichromate of potash, washed, passed in chlorine, and soaped. These two specimens were left for a whole night in hydrochloric acid at $1\frac{1}{2}^{\circ}$ Tw., at about 60° F.

It may be seen that the first is completely green, while the second has changed so little that the difference cannot be observed at a little distance; it appears as a fine black.

In further searching for the cause of the greening of aniline black, we were led to make the following experiments which, in combination with those given above, support the conclusions of this short paper :—

We steeped a specimen of black, printed with the tartrate and fixed in carbonate of soda, in a solution of muriatic acid at about 3° Tw., and afterwards washed in distilled water. A portion was placed in a hot liquid containing chlorate of potash and hydrochloric acid. The green at once changed into a fine black.

Another specimen of black made green by hydrochloric acid and washed in distilled water, was steeped in a weak and cold mixture of chlorate and acid, and became restored to a good black. A specimen of black, not previously turned green by acid, was put into the same solution; the black remained good, not undergoing any change in shade.

A specimen of black was put into contact with sulphuretted hydrogen, it became green at once. This sample exposed to air and light returned to an intense black.

The action of sulphuretted hydrogen is more apparent upon a damp than upon a dry specimen. A black which has gone through the starching and finishing operations is less quickly acted upon by sulphuretted hydrogen; but in every case the black eventually becomes green.

The hydrosulphite of soda acts upon the black like sulphuretted hydrogen.

In the presence of an excess of caustic soda, the hydrosulphite of soda reduces the black; but in this case the black is restored by long exposure to the air.

A specimen of black made green by sulphuretted hydrogen, washed in distilled water, and placed in a jar of oxygen, is immediately brought back to its original colour.

Another specimen made green by muriatic acid, washed in distilled water, and put into oxygen gas, was restored to an intense black.

Another specimen made green by muriatic acid was immediately restored to black by placing it in a solution of chlorine gas.

Conclusions.—The question of aniline black should be looked at from three points of view :—

(1) What is the theory of the production of aniline black upon cotton cloth ?

(2) What are the influences which cause the black to become green ?

(3) What are the best means of assuring the stability of aniline black and preventing greening ?

(1) Aniline black is obtained upon cotton by a successive oxidation in layers (*couches*) of the aniline.

(2) The change of the black to green appears to be due to some action which takes a certain quantity of oxygen from the aniline.

(3) The best means of assuring the stability of the black and to diminish the action of greening is to promote the intimate combination of the aniline with oxygen ; that is to favour the oxidation or oxygenation of the aniline.

In practice, the means of oxidation are prolonged by hanging in the ageing rooms heated as high as 100° F., the action of bichromate, alkaline hypochlorite, and even steaming.

The passage in carbonate of soda does not add to the intensity of the black.

It is proper to add that the nature of the aniline salt is not unimportant, either for obtaining a complete fixation of the aniline or for avoiding the serious danger of tendering the cloth.

We now pass on to the paper of M. R. Glanzmann, which is entitled "Note upon the Black from the Muriate of Aniline." The author says :—

The stability of aniline black upon vegetable fibre depends upon—

(1) The composition of the colour.

(2) The oxidation.

(3) The raising and auxiliary treatments which are given to develop the black.

With regard to the composition of the colour, we may observe the following facts :—

If the colour is too acid it gives a black which soon becomes green when exposed to the action of air, moisture or acids. If the aniline salt is too low in quantity, or not properly oxidized in the colour, the same defect is observed.

The thickening has a great influence upon the fastness of the black. Many thickenings prevent the development by masking the salts ; when the quantity of colour deposited on the fibre is too small, or when the colour is too thick, the blacks obtained are not so fast.

Black printed by hand-block is more stable than roller-printed black, even when the roller colour is made a fourth stronger, and the conditions are the most favourable possible. Iron salts favour in a high degree the development of the black, but the colour is not so fast.

If the black be oxidized at a low temperature, say between 50° and 60° F., or if the oxidation is carried on too rapidly, the colour produced is very sensitive.

A slow and gradual oxidation alone can yield the most stable black ; one or two days' cool hanging after printing, and then a dozen hours of oxidation at 77° F. for the dry, and 72° F. for the wet bulb, has given us the best results as to beauty and fastness of colour without tendering the cloth.

Simply washing off the thickening and saturating the acids is not sufficient to give a good black, it is necessary in this operation to complete and perfect the oxidation ; this is accomplished by means of bichromate of potash, and the hypochlorites of lime and soda.

The greening of the black is not a deoxidation ; if it was, the action would be of a quantitative nature, that is to say, a certain definite amount of acid would make green a definite and constant quantity of aniline black.

Reducing agents, as the hydrate of protoxide of iron, glycerine, zinc powder, etc., have no action upon the black.

The reduced shades of aniline black cannot resist in the least degree the greening action of acids.

Pure salts of aniline give the finest black; mixed salts give blacks less beautiful and less solid.

Contrary to the opinions of many, we believe that there is but one aniline black, and that its fastness or stability is in direct proportion to the quantity of it which is applied upon a given portion of cloth. The development of the black can be easily followed through its different stages.

As soon as a green shade is visible upon the fibre there is production of aniline black; but on account of the small quantity of it formed it is not fast; the quantity of black can be observed gradually increasing, for under proper conditions the colour becomes light green, dark green, and finally bronze colour. These three shades correspond, after washing off, to three different blacks as regards stability and appearance.

The light green gives a true blue colour, the dark green a blue-black, and the bronze an intense black, which can be modified to a dark brown-black by strong oxidizing agents; this latter is the fastest black.

Conclusions.—Blacks from aniline salts always become green when placed in contact with acids or acid salts.

Alkalies restore the black colour.

This reaction is a characteristic feature of aniline black, just as the reactions of litmus, annatto, etc., which change colour by contact with acids and alkalies.

The more intense the black, in other words the greater quantity of it which is deposited upon a given point, the less visible is this property of it, and the more resistant and stable the colour.

To obtain a fast aniline black, or one the least liable to become green and lose its brilliancy, the following conditions must be satisfied:—

As large an amount as possible of neutral salt of aniline must be in the colour, representing 10 to 16 oz. of pure aniline per gallon of colour.

The oxidation must be quite complete before washing off or raising.

Lastly, the black must have a final development by power-

ful oxidizing agents, applied during or after the cleansing from thickening.

Among the specimens brought to support these statements, a black made from a mixture of chlorate and muriate of aniline shewed the best colour both as to excellence and stability. This mixture permits the production of a very intense black, without any damage to the cloth. It resists the action of dilute muriatic acid.

The muriate of aniline mixed with muriate of naphthylamine, gives a black which is not easily turned green; but if there be much naphthylamine, the black is dull, and the whites are not good.

The black made with iron gives the worst results; it becomes green very readily; the nitrate and chloride of iron also tender the cloth.

So far M. Glanzmann. We next come to a paper of M. J. Dépierre upon the same subject. He says:—

The question which the chemical section of the society submitted was as follows:—

To enquire what are the causes of aniline black becoming green, and above all, what practical means are there for remedying this defect.

Before entering upon the subject, I believe it will be useful to recall the opinions which have been expressed upon some of the known properties of this colour.

According to a writer in Wurtz's *Dictionnaire de Chemie*, "aniline black is a unique product, it becomes dark green by contact with acid, and also by long exposure to air. A simple washing (?) restores it to its original colour. It is insoluble in all the usual chemical agents; the strongest sulphuric acid does not act upon it. Nitric acid changes it into picric acid. Upon fibres it possesses very great stability, withstanding the action of boiling soap, and supporting the strongest treatments of the madder styles."

According to another authority,* it is the product of the action of a powerful oxidizing mixture upon a *mixture* of aniline and toluidine. It is not a definite compound, but

* Girard et Delaire, 1873, p. 623.

composed of several matters, green, blue, and brown. It is insoluble in water, alcohol, ether, benzine, soap, alkalies, and acids. Acids change its colour to green, and alkalies bring the colour back again. Dilute bichromate of potash increases the intensity of the colour, more concentrated it reddens it.

"Chlorine and the alkaline hypochlorites destroy the colour after a time. However, according to M. C. Koechlin, when the action of bleaching powder upon the colour has not been too prolonged, so that the colour is not completely destroyed, but brought down to a reddish chocolate, a remarkable phenomenon occurs. The original black colour, little by little reappears, and in time comes out as strong as it was before it was subjected to the action of the bleaching powder." *

According to M. Georges Witz, chloric acid completely bleaches the blacks, but only when in concentrated solution.

Most authorities agree that the black becomes green under the influence of the vapour of water.

Reducing agents for the most part have no action upon the black; but a curious effect is produced by the hydrosulphite of soda. A specimen of cloth printed with aniline black, finished, being treated with hydrosulphite of soda becomes grey; if afterwards it be treated with weak solution of bleaching powder the black returns. This change can be effected several times in succession.

By treating a specimen of the black with a mixture in powder of equal parts of bichromate of potash and oxalic acid, and exposing it to the action of very moist steam, a reddish brown matter is formed (there is of course much chromic acid). If the sample be dried there is an effervescence, and the black totally disappears. The parts not completely decolourized do not change if treated with ammonia. If a little bleaching powder be added there is a complete bleaching. It is known that indigo is bleached by this treatment as also by action of the red prussiate and caustic alkali, but the two latter substances have no action upon the black.

The acids which act most powerfully upon the black fixed

* See Girard et Delaire, p. 628, and *Moniteur Scientifique*, vii, p. 769.

upon fibre by changing it to green are sulphurous acid and hydrochloric acid. Carbonic acid has no sensible action, but acetic acid in the gaseous state acts nearly as strongly as hydrochloric acid.

Kopp states that the black is a single substance, the shade of which depends upon the acidity or neutrality of the colour.

Brandt believes there are two blacks, the one formed by chlorine and substitutions of chlorine, the other by the oxidation of a salt of aniline.

M. Georges Witz considers that there are two particular kinds of green in the same black, the one a bronze green, which is easily changed to black by alkalies, the other a yellow green produced by the action of sulphurous acid, and which cannot be changed back without the intervention of oxidizing agents. The yellow-green is produced immediately in the cold by a solution of sulphurous acid, containing not more than one-thousandth part of acid.*

The effect of greening produced upon printed aniline blacks is owing to the different actions cited above. Thus it is known that illuminating gas contains frequently, not to say always, products of sulphur, which by burning give sulphurous acid. This acid acts upon the edges and exterior folds of goods exposed for sale, and makes them green. An annoyance from the same cause was reported from Manchester eighteen years ago, in connection with the murexide colour, and it is probably from this cause that the English printers do not employ aniline black on so large a scale as we do.

The quality of the finishing materials must be taken into consideration, for it frequently happens that they contain salts, which by contact with the moist atmosphere of warehouses and shops undergo change, and then acids become free, which act upon the colour.

In damp places it may be observed that points and stains of a more or less considerable size are in time produced upon finished aniline blacks. Upon these places an acid is

* *Moniteur Scientifique*, 1871, p. 75; *Bull. de Mulhouse*, 1872, p. 354; *Bull. de Rouen*, 1873, p. 76.

formed, probably due to the vegetable growth which takes place.

Another cause of greening well-known to printers is fog. As the greater number of manufactories are situated in damp valleys, and as there is a large consumption of coal and hydrochloric acid, the fog becomes charged with sulphurous acid from the consumption of coal, and also with vapours of hydrochloric acid, which act very quickly upon aniline black, especially upon the pieces hung up to air before the starching.

In the daily use of those prints employed as clothing, the acid cutaneous exhalations produce a rapid greening of the black, and this effect, though only momentary, has led to a distrust of the fastness of the colour, which is really one of the fastest known.

Finally, the prolonged action of the solar rays *appears* to turn the black green independently of the other causes given.

It is admitted that the method of formation of the black, and its intensity have an influence upon its greening; that is to say, the weaker it is the easier it becomes green. A black oxidized at a low temperature is more sensitive than one oxidized at a high temperature.

Taking this as a starting point, I have made a series of experiments with different blacks.* I have especially examined if it were possible to produce, by varied treatments, a strong resisting black from a relatively small amount of aniline in the colour. Colourists know that by increasing the

* (1) Blacks with muriate of aniline containing 60 of salt, or about 42 of aniline per 1,000 of colour.

(2) Blacks with muriate of aniline containing 75 of salt, or about 53 of aniline per 1,000 of colour.

(3) Blacks from the same, with 90 of salt, or about 63 of aniline per 1,000 of colour.

(4) Blacks with tungstate of chromium, containing 53 of aniline per 1,000 of colour.

(5) Blacks with muriate of aniline, containing 63 of aniline and 20 of muriate of naphthylamine per 1,000 of colour.

(6) Steam black with prussiate of ammonia, containing 80 of aniline per 1,000 of colour.

(7) Black with tartrate of aniline, containing 90 of aniline per 1,000 of colour.

(8) Black with nitrate of aniline, containing 125 of aniline per 1,000 of colour.

proportion of salts, and using up to $22\frac{1}{2}$ oz. of aniline per gallon, it is easy to obtain blacks so little sensitive that they may be called resistant blacks. But in this practice the cost price and the difficulty of avoiding a weakening of the cloth are grave objections. (In speaking of $22\frac{1}{2}$ oz. of aniline, I mean by that the quantity of aniline which actually goes to form the black and is fixed upon the cloth.)

Whatever operations I submitted these various trials to, the resulting colour was always turned green by the action of hydrochloric acid at 3° Tw. in ten hours, and of sulphurous acid gas at a temperature of about 60° F. for the same time. It was, however, observed that the muriate of aniline blacks became green easier than any of the others. The black made with nitrate of aniline at 125 for 1,000 of colour* resisted well, but none so well as the black with prussiate of ammonia.†

* That is $1\frac{1}{4}$ lb. per gallon. The French reckon so many grammes per litre of 1,000 grammes measure; the numbers can be turned into pounds or ounces per gallon by recollecting that a gallon is 10 lb. measure. Thus 100 grammes per litre (1,000 grammes) is evidently 1 lb. per gallon; 80 grammes per litre is $12\frac{8}{10}$ oz. A convenient rule to bring the grammes per litre into ounces per gallon is to multiply 16 by the number of grammes, and cut off two figures to the right as decimals; thus 140 grammes per litre is $140 \times 16 = 2240$ oz. per gallon, taken above as $22\frac{1}{2}$ oz.—*Ed.*

† This black, as communicated to the Chemical Section by M. Justin Schultz in 1873, is made as follows:—

4 lb. white starch.
2 lb. pale British gum.
3 oz. soot.
2 gallons water; boil and add
2 lb. 10 oz. chlorate of baryta (or $2\frac{1}{4}$ lb. chlorate of potash); when cold
add
 $5\frac{1}{2}$ lb. tartaric acid dissolved in 1 gallon hot water; then
8 lb. prussiate of ammonia.
 $4\frac{1}{4}$ lb. aniline oil.

Prussiate of Ammonia.

$9\frac{1}{4}$ lb. sulphate of ammonia.
1 gallon water.

Dissolve

26 lb. yellow prussiate.

$5\frac{1}{4}$ gallons water.

Mix, and leave two days to crystallize.

[To be continued.]

9. *British and Foreign Patents, from the Commissioners of Patents Journal, Aug. 29th to Sept. 22nd, 1876, inclusive.*

Printing Rollers; Printing, Bleaching, and Dyeing Apparatus.

3569. HENRY WILDE, of Manchester, in the county of Lancaster, Engineer, for an invention of "Improvements in the manufacture of metal rollers for printing calico, and for other purposes."—Dated 12th September, 1876.—Provisional protection has been granted.
3473. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, for an invention of "An improved method of and machine for printing woven and other fabrics."—A communication to him from abroad by Eugène Boeringer, of Paris, France.—Dated 2nd September, 1876.—Provisional protection has been granted.
2933. WALTER MACLEAN, of Glasgow, in the county of Lanark, North Britain, for an invention of "Improvements in printing, lithographing, or zincographing on textile fabrics."—Dated 6th September, 1873.—This patent has become void.
3018. JEAN PÉRINAUD, Chemist, and JUSTIN MARCHAL, Dyer, both of Paris, France, have given notice to proceed in respect of the invention of "A process of supplying dyed silk fabrics."
2997. SAM MASON, junr., of Manchester, in the county of Lancaster, and MICHAEL ALCOCK, of Pendleton, in the same county, for an invention of "Improvements in kiers employed in the bleaching, scouring, or treatment of woven fabrics, yarns, and other materials or substances."—Dated 12th September, 1873.—The £50 stamp duty has been paid upon this patent.

Wool Treatments.

2016. HENRY EDWARD NEWTON, of the Office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, has given notice to proceed in respect of the invention of "An improved process and apparatus for removing pieces of

straw, wood, and other vegetable substances from fabrics made of wool, silk, hair, or other animal fibres."—A communication to him from abroad by François Delamare the younger, of Paris, in the republic of France.

3509. JONATHAN HOLDEN and JOHN EDWARD HOLDEN, both of Reims, France, Wool Combers, for an invention of "Improvements in machinery for washing wool and other fibrous material.—(Complete Specification.)—Dated 6th September, 1876.

Finishing Operations.

1845. JOSEPH HOWARTH, of Rochdale Road, Manchester, in the county of Lancaster, Plumber and Glazier, has given notice to proceed in respect of the invention of "Improvements in apparatus for heating the cylinders of machines for calendering, mangling, and drying."
1987. HENRY EDWARD NEWTON, of the Office for Patents, 66, Chancery Lane, in the county of Middlesex, Civil Engineer, has given notice to proceed in respect of the invention of "Improved apparatus for applying starch or other analogous preparation to various articles made of textile substances."—A communication to him from abroad by Thomas Shires Wiles and Alonzo Pelton Adams, both of Albany, in the state of New York, United States of America.
2585. GEORGE HENRY NUSSEY and WILLIAM BRADSHAW LEACHMAN, both of Leeds, in the county of York, for an invention of "Improvements in machinery or apparatus for pressing woollen and other woven or felted fabrics."—Dated 1st September, 1869.
3324. JOHN STEVENSON KERSHAW, of Littleborough, in the county of Lancaster, for the invention of "Improvements in apparatus for stretching woollen or mixed woollen and cotton cloths, which apparatus is to be used in conjunction with 'tentering' machines for drying woollen cloths."—Provisional protection has been granted.
3353. SAMUEL GIBSON RHODES, of Park Street, Leeds, in the county of York, Gentleman, for an invention of "Improvements in finishing yarn and fabrics and in apparatus connected therewith."—Dated 26th August, 1876.—Provisional protection has been granted.

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[Vol. II.

1. Cantor Lectures on Wool Dyeing.

THE third course of Cantor Lectures of the Society of Arts for the last session was upon Wool Dyeing, and was delivered by Mr. George Jarman, in the months of March and April last. These lectures are being published in the current numbers of the Journal of the Society of Arts, and we are indebted to that publication for being able to give a resumé of them. Very little original matter has appeared in England upon the subject of wool dyeing, and most of what we possess consists of empirical receipts for obtaining certain shades of colour. We therefore heartily welcome the appearance of these lectures, which we are sure will in an eminent degree fulfil the object which the Council of the Society of Arts had in view when instructing Mr. Jarman to give these discourses, which, as explained by the lecturer, was, "that students preparing for examination in this subject may have indicated to them the course of study which it is desirable for them to follow." Much of the matter is necessarily of an elementary nature, such as may be found in manuals upon chemistry and general dyeing, but there is also much which is eminently practical, and with which none but those specially engaged in woollen dyeing can be familiar. It so happens in England that the dyeing of the different fibrous matters forms distinct trades, carried on in different districts, and though they have much in common, it is seldom that the cotton dyer is acquainted with the peculiar processes of

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either the woollen or silk dyer. Each in his own department seeks to perfect his processes in an independent manner, and it has not unfrequently been found that the arrangements of apparatus and treatments of materials which have for long periods been profitably applied to a particular fibrous substance, were, when known, capable of being applied advantageously to one or both of the others. It is clearly desirable that those engaged in the dyeing arts should extend their knowledge as far as possible in every direction, and not be content to confine it to the particular material they are usually occupied upon, seeing that valuable hints may be obtained from the practice of the dyers working upon an entirely different substance.

After some judicious introductory remarks upon the use which practical dyers would find in a knowledge of chemistry, Mr. Jarmain proceeds to treat of water.

Water for Wool Treatments.—Mr. Jarmain has the following as the conclusions he has come to upon the general character of a water suitable for wool :—

“Having had a large number and great variety of waters to examine from time to time, in order that their suitability for woollen manufacturing purposes might be ascertained, I have arrived at the following results, which I may term limits of impurity in water suitable for wool scouring and dyeing. The water must fulfil the following conditions :—

1. It must not exceed 7 degrees of hardness by Clark's soap test, of which it should lose not more than 2 degrees by boiling for an hour, and returning the water evaporated.
2. It must not deposit a brown sediment of oxide of iron when exposed freely to the air for some hours, nor must it give a blue colouration when a few drops of a solution of red prussiate of potash are added to a portion of it.
3. A portion of the water contained in a white glass bottle, to which a few drops of a solution of logwood are added, should be coloured of a sherry colour, which

may be compared with a portion of distilled water treated in the same way.

4. The water should be clear, and must not throw up a brown scum of oxide of iron or organic matter when heated up to the boil.

5. Samples of wool or woollen fabric mordanted and dyed with the colours required, should compare well with similar samples mordanted and dyed with distilled water, or any other water known to be good.

A water which fulfils the above conditions is suitable for scouring and for the dyeing of woollen colours. Any considerable departure from these conditions will be attended with unsatisfactory results, unless the water be submitted to some treatment or purification."

The lecturer next enters upon the details of the application of the soap test to water, with the table of degrees of hardness, soap test measures, and differences which may be found in many books. We do not say that it is a matter of importance in such a lecture that Mr. Dugald Campbell's observation upon the perturbation caused by presence of magnesian salts in water should be passed over, for these salts are seldom found in sufficient quantity in water not exceeding 7° of hardness to sensibly influence the results. But at the present day manufacturers are boring deeper for water than was customary a few years ago, and we have had many occasions to corroborate Mr. Campbell's statement that in the presence of a certain proportion of magnesian salts the soap test is quite delusive and shews a degree of hardness, not as stated by Mr. Jarman to be the absolute or total hardness caused by the lime or magnesian salts, but actually less than is owing to the lime salts alone. Every sample of deep well water that we have analyzed from the red sandstone which abounds in Lancashire contains sufficient magnesia to completely invalidate the soap test as indicating the amount of lime in the water, and it may be safely concluded that the results will be deceptive as applied to practical operations, for though a calcareous water froths or lathers in the test bottle with less soap when it contains magnesia than without it, it seems

certain that when applied in scouring both the magnesia and the lime will destroy soap. It is not apparent at first why the water of 7° of hardness should, to be good, only lose 2° by boiling as laid down by Mr. Jarmain. It would seem from this that the presence of carbonate of lime is more injurious than sulphate of lime, a conclusion which we believe is not usually admitted for either dye water or a scouring water, but further on the reason is given.

We think also that Mr. Jarmain claims too much for the logwood test. He gives the following table of reactions as observed when a few drops of decoction are added to the water.

“The following reactions will be observed :—

Distilled water	A brown amber or sherry colour.
Water containing only—	
Calcic sulphate or chloride..	Red amber becoming red brown.
Magnesia do. ..	Amber becoming more brown.
Calcic bicarbonate.....	Red claret passing to a bluer shade.
Magnesia do.	Red claret becoming more blue.
Ferrous bicarbonate or sulphate	} Olive black becoming blue black.
Alkaline carbonates, carbonate of potash or soda.....	
Free acids	} Dark cherry.
	Light amber.

The depth of colouration is in each case in proportion to the amount of the special impurity in solution. When there is a mixture of impurities the colouration partakes also of a mixed character, but a departure from the standard of distilled water is readily recognised, and should not be considerable.”

We much doubt whether logwood is of any use except as a convenient test for iron in solution; as a distinguishing reagent for different magnesian or lime salts its indications are all but worthless, and for acidity and alkalinity we have far better tests. For practical purposes however, the method of examination proposed by Mr. Jarmain would doubtless give a very good idea of the relative value of a given water. We give in full the remarks upon the influence of the various

impurities in water, in scouring and dyeing, which are of great value and practical importance.

"Calcareous and Magnesian Impurities.—Influence on Scouring with soap.—These impurities, in whatever form they may be present in the water, decompose and destroy as a detergent their equivalent quantities of soap, by converting it into a lime or magnesia soap, which is insoluble and greasy, and not only non-detergent, but it adds to the difficulty of the subsequent thorough cleansing. Every pound of chalk or carbonate of lime dissolved in water destroys 10 lb. of soap. The insoluble soap so formed cannot be washed out from the wool or fabric, to which it attaches itself with great tenacity, and is frequently very mischievous in the dyebath, producing irregularity in the reception of both mordant and dye. I have therefore mentioned 7 degrees of hardness as the furthest limit at which it will be found advisable to employ water for scouring purposes when soap has to be used.

Even during the rinsing or washing off the wool or fabric where soap has been used, the mischief is increased by the fresh water acting upon the excess of soap which has to be used to obtain a scour; this excess is also converted into insoluble soap, and is added to that already formed.

Influence on Scouring with Alkaline Carbonates and Urine.—Calcareous and magnesian salts, when heated up with alkaline carbonates, precipitate their carbonates in a powdery condition which may readily be removed by washing, but as wool generally contains a portion of natural fatty matter which forms a soapy emulsion with the alkaline carbonate, the presence of calcic and magnesian compounds interferes with the detergent action of the alkalies. The bad effects, however, are not so great as when soap has to be employed for scouring.

Influence on Mordanting and Dyeing.—Calcic and Magnesian salts, when in the condition of sulphates or chlorides, appear to have no influence over the reception

of either mordant or dye; waters containing them act, so far as woollen dyeing is concerned, as pure water.

When the salts are in the condition of carbonates, held in solution by carbonic acid (so called bicarbonates), they are often exceedingly troublesome.

1. They diminish the effect of the mordant, and necessitate great care in counteracting this evil tendency by the use of an acid or tartar.

2. They produce a different shade of colour in most cases in the dyebath, and require great skill and experience to obtain uniform results.

In fact, the dyer has a host of complaints to make against these earthy carbonates, for they blue his cochineal scarlets and purples; they blue the reds of his red woods; they strengthen the colours of logwood, fustic, and bark, but at the same time, the colours lose their brightness, and the strength of colour is not permanent; they destroy his tartar, which expends itself in converting the earthy carbonates into tartrates; they act generally as a diminution of mordant.

Impurities in the form of Iron Salts (Ferruginous Waters).—Their influence on Scouring.—With soap they act like the calcic and magnesian salts, producing an iron soap which adheres to the wool, and is more mischievous than even the lime and magnesia soaps, for it seriously affects the colours afterwards dyed upon the wool. With alkaline carbonates (soda ash, urine) the oxide or hydrate of iron is precipitated, which adheres more or less to the wool or fabric, and is a constant source of anxiety and annoyance to the dyer.

Their influence on Dyeing.—As iron compounds always have the effect of saddening colours, it is hopeless to expect to obtain any bright shades of colour when a ferruginous water is used. Even with the dark and sad shades, and blacks, the use of this description of water frequently produces unsatisfactory colours. I have often seen cloudy and rusty spots on pieces which have been dyed with such water.

Impurities in the form of Alkaline Carbonates.—*Influence on Scouring.*—When the water is not also charged with earthy carbonates, the presence of these carbonates is beneficial rather than otherwise in scouring with either soap or alkaline carbonates.

Influence on Dyeing.—I know of no condition of water which is more troublesome to the dyer than this alkaline condition. In the mordanting they precipitate the bases of iron, tin, and copper salts, and of alum, and reduce bichromate of potash to the condition of yellow chromate, a much less effective mordant. They act on mordants in a similar manner to what the earthy carbonates do, but the action is sharper and more decided. Their evil influence can only be prevented by the use of an acid to neutralize the alkalinity of the water.

In the dyeing with this alkaline water the greatest care and skill are required, otherwise the colours will be affected, and in the rinsing or washing off, the colours, which may have been set right in the dye bath, will be thrown altogether wrong again by the alkalinity of the wash-water.

I repeat, I know of no condition of water which is more perplexing to the dyer than this alkalinity; and, unfortunately, it is of too common occurrence in some of the woollen districts of Yorkshire, where the dyer derives his supply from wells, or by boring into the lower beds of the coal measures, which appear to be charged with carbonate of soda."

It is perhaps not generally known that waters of this character are in actual use in Yorkshire; we had occasion lately to examine a sample of water from near Bradford in that county, which certainly had a surprising constitution, and, as we were not at first informed of its origin or the locality from which it came, we believed it to be some medicinal water. It contained about 32 grains of solid matter per gallon, and shewed about $1\frac{1}{2}^{\circ}$ hardness to soap test, there was hardly a trace of lime present, nearly the whole being soda salts, among which a considerable proportion of car-

bonate. Such a water would be very suitable for bleaching and scouring operations, but we can easily imagine, never having had practically to deal with such a water, that it would present immense, and, we might say, absolutely insuperable, difficulties in many styles of dyeing, and, for many colours, in any style of dyeing. For simply dyeing or mordanting the alkalinity could be easily corrected by addition of acid, but, as Mr. Jarmain observes, the washing off and rinsing would be the difficulty, all fine or light shades being liable to be utterly changed and spoiled by it.

“Organic Impurities.”—Waters charged with organic matters, in sufficient quantity to give them a colour, are not suitable for bleaching wool, as they tend to stain it; but I have not met with any cases in which they have proved prejudicial for scouring or dyeing, except the organic matter be in the form of dye-waters from other works. Even the peaty waters from our Yorkshire moorlands do not seem to have any prejudicial influence on the dyeing of wool or woollen fabric; at any rate, no cases have come under my notice.

Impurities in the form of Free Acids or Acid Salts.—I have met with two classes of these waters:—(a) Waters containing peaty acids. (b) Water running from pyritic shales near the surface, which by oxidation charge the water with sulphate of iron. On exposure, much of the iron deposits leave the water acid with free sulphuric acid. Both these waters are exceedingly injurious to steam boilers. The acids become concentrated by evaporation in the steam boiler and attack the iron plates.

A new boiler, for which the first class of water was used, had its half-inch plates perforated after three months' use, and the tubes of a multitubular boiler had to be removed after using the second description of water for a few months. Both waters were entirely corrected by the addition of a little lime. They neither of them contained a trace of lime.

These waters are unsuitable for the treatment of wool. The second one decomposes soap, and liberates the fatty

acids contained in it, which attach themselves to the wool in the same manner as the lime and magnesia soaps which I have already described."

With regard to the treatment of impure waters, to purify them for use, Mr. Jarmain says truly it is "always troublesome, costly, and unsatisfactory;" it should only be undertaken when it is found impossible to get a better supply. He gives the filtration process and Clark's softening process, both of which are well known in the manufacturing districts; he quotes also a process applied by Dr. Gunning, with success, to the turbid waters of the river Meuse. "For the treatment of 3,000 gallons:—1 lb. dry perchloride of iron is dissolved in water, and then thoroughly mixed with the bulk; 1 lb. of soda ash of 52 per cent. is dissolved in water, run in, and the whole again agitated. The hydrated peroxide of iron deposits, carrying down with it the organic impurities, common salt being the only substance left in solution."

For the treatment of permanently hard waters Wanklyn's method is given, as well as the soap treatment.

*"Treatment of Permanently Hard Waters (Wanklyn's Method).—*As has already been explained, these waters contain the sulphates of lime and magnesia, which have always proved to be the most difficult of removal. Mr. Wanklyn has recently proposed to soften waters of this class by first adding bicarbonate of soda and then lime. The bicarbonate of soda first converts the sulphate of lime into bicarbonate of lime, and the subsequent addition of lime precipitates the bicarbonate so formed. Sulphate of soda remains in solution in the water.

I have not had an opportunity of seeing this process tried on a large scale, but I consider it likely to accomplish the end in view, if its cost should not prove to be a bar to its use.

Treatment of Hard Waters with Soap.—If hard water must of necessity be employed for scouring with soap, it is advisable to separate the hardening matter, by mixing a sufficient quantity of a hot solution of soap with it, and then causing it to run through a filter-bed before use.

The insoluble soaps will thus be separated without attaching themselves to the wool or fabric, and they may be collected and treated with hydrochloric acid, to decompose them and separate the fatty acids, which may then be collected and reconverted into soap, by boiling them up with caustic or even carbonate of soda, and the soap thus obtained may be used again for the same purpose. Water thus treated is well adapted for the scouring of wool and woollen goods."

For the correction of water in dyeing and for a proposed method of treating refuse water from woollen mills we have the following:—

"Treatment and Correction of Waters in the Dye-bath.—

Organic matter, oxide of iron, and often a considerable proportion of the hardening matter, may be caused to rise to the top, and may then be skimmed off, by dissolving alum in the water in the proportion of about 4 oz. per 1,000 gallons, and then raising it to near its boiling point.

In preparing waters which contain alkaline or earthy carbonates or bicarbonates, as a bath for either mordanting or dyeing, they should be treated with sufficient sulphuric acid to expel all the carbonic acid, and to neutralize any alkali which may have escaped washing out from the scour.

The use of bran is frequently serviceable in removing impurities from water in the bath.

Purification of the Refuse Waters from Woollen Mills.—In concluding my remarks on the subject of water, I beg to draw attention to the fact that the refuse-waters from a woollen manufactory contain within themselves the elements of their own purification. At the present time, the practice is to turn these refuse-waters into the river-courses as they are done with. Sometimes mordant-baths are run out; at other times the spent dye-baths, and soap, or alkaline fluids. These mingle in the common receptacle, the river, and precipitate each other there, thus producing those black

deposits which give to our streams in the woollen districts such an inky and foul appearance. I have mixed together solutions of all the substances used in our woollen industries, and find that they precipitate one another, and leave the supernatant water in a tolerably clear condition. The remedy seems to be, so far as the woollen trade affects the purity of the rivers, to run all the liquids into one common reservoir, and, after subsidence, to pass, if necessary, the supernatant water through a filter-bed into the river. The utilization of the black muddy deposit would, I believe, speedily follow."

For scouring wool, stale urine is still employed by many manufacturers; ammonia is also used, that being preferred which is distilled from urine. "The strength of the ammonia is determined by taking its specific gravity by means of a hydrometer, called an ammonia meter. The one in common use in Yorkshire and Lancashire has an arbitrary scale, each degree equalling 3, water being taken at 1'000. Thus, the specific gravity of ammonia at 20 degrees equals 1'000— $(20 \times 3) = \cdot 940$." In gas tar ammonia the hydrocarbon impurities are said to act strongly on the skin of the workmen, and the sulphides act injuriously on the wool.

Carbonate of soda is, however, the most generally used detergent, and Mr. Jarmain gives the method of testing the value of soda compounds by the usual alkalimetical method. Soap of course is employed, and silicate of soda is said to be coming into favour;—"it cleanses the wool very satisfactorily, and leaves it in a suitable condition for the reception of dyes, particularly those of the aniline colours."

We give what Mr. Jarmain says upon the practice of wool, yarn, and cloth scouring:—

"Wool Scouring.—The detergents used are, soft soap for fine long wools; and for short wools, both coarse and fine, urine alone, or urine and soda ash, or soda ash alone, silicate of soda, and various mixtures of alkaline carbonates and soaps.

The best temperature for the scouring of loose wool is from 125° to 135° F.

The old-fashioned mode of scouring wool, and which gives fair results, is to work it about in a kettle or tub containing the scouring liquid, with a stick or stang, for five or ten minutes, and then lift it out upon a scray, with the stang or a fork, by small portions at a time. When it has drained upon the scray, it is then thrown into a cistern called a 'wash-off,' the bottom of which is fitted with perforated iron plates. Water is then run into the cistern by a 5 or 6 inch pipe entering horizontally, and when full the wool is stirred up well in it. The water is then let out from under the perforated plates by means of a clack. The washing with water is repeated two or three times. This method requires an abundant supply of water, but is in other respects economical. An improvement upon this process, very often resorted to, is to have a perforated sheet iron shell swung on a trunnion, and fixed to a crane. The shell is lowered down into the scouring pan, and the wool scoured in it; when ready it is drawn out by the crane and the wool thrown out into the wash-off cistern by tilting the shell over. The wool is washed two or three times as before. One man can scour from 500 lb. to 600 lb. per day by the first mode; it requires two men to scour by the perforated shell, but more work can be got through.

For certain classes of wool, in which soap is employed as the detergent, the scoured wool is passed between rollers instead of washing it.

Long stapled wools are manipulated with forks by hand in the scouring fluid.

In most large factories, however, the above processes for cleansing wool from their natural impurities have been superseded by the introduction of wool scouring machines, the first of which was invented in 1851, by Mr. John Petrie, jun., of Rochdale, who has since that time very greatly improved the machine; in fact, the latest form of it, the 'Paragon,' as he calls it, leaves little to be desired.

A complete machine consists of three boxes or bowls. The wool is fed into the first by a boy. In this bowl a strong scour is placed, through which the wool is forked by forks ingeniously fixed to cranks; from this bowl it is passed through rollers into the second, which contains a weaker scour; it then passes through rollers to the third, in which it is forked through running water; and lastly passes between heavy squeezing rollers and is thrown forward by a powerful fan which leaves it light and open. The wool is turned out very clean and half dry. In fact the machine performs a large amount of work in a very satisfactory manner, and the manufacturers who use them tell me that they are very much pleased with them. Mc.Naught's and Leech's machines, each possessing special features of their own, are also spoken well of by those who use them.

Yarn Scouring.—The impurities to be removed by scouring from woollen yarns are, oil which has been used to enable the wool to be scribbled and spun, and accumulated dirt. The detergent used is a mixture of soap and ammonia, but for some descriptions of yarns cheaper alkaline liquids may be used.

It is important that the felting of the yarn should be avoided as much as possible. This may be accomplished by steeping the yarn in hot water and leaving it to cool before scouring.

The scouring is done in a wood cistern filled with the scouring fluid; the yarn is hung on sticks placed across the cistern, it is turned over frequently, and worked about in the scour, and finally wrung out. The best temperature for the yarn scour is from 140° to 150° F.

Cloth Scouring.—This is always done in a machine consisting of a bowl or cistern, and squeezing rollers placed above. The scouring materials vary with the description of cloth, soda ash, soda crystals, and soap ash being usually employed for woollen cloths. The cloth passes through the scouring liquid heated from 150° to 160° F., and then between the rollers for some time,

whereby the oil contained in the cloth is removed in the form of an emulsion by the detergent. The scour is frequently used again, after being strengthened by the addition of more alkali. The cloth is finally washed in clean running water on the machine for a considerable time. The thorough removal of all oil, soap, and grease from the cloth is very important for the subsequent dyeing, for if any remain in it, the action of the mordant is seriously interfered with."

In the sulphuring of the wool it appears that the ancient process of hanging up in a room in which sulphur is burned is very generally used. This is usually known as gas bleaching to distinguish it from bleaching by sulphurous acid dissolved in water. The methods of "liquid bleaching" are given as follows:—

"The solution of sulphurous acid used for bleaching purposes is one of the following:—

1. A solution of the gas in water.
2. A solution containing from 3 to 5 per cent. of bisulphite of soda, to which an equal volume of hydrochloric acid is added.
3. A solution, containing from 3 to 5 per cent. of the bisulphite, from which the sulphurous acid is set free in a subsequent operation.

The wool to be bleached should be well scoured with soap, washed, and steeped in one of the above solutions for some hours. If the first or second solution be employed, it will only require to be washed to free it from the acid; it may then be placed in a coach, and covered up with a sheet for some time, under which circumstances the bleaching action will be continued by the sulphurous acid remaining adhering to the wool.

If the third solution be employed, the wool, after draining, should be passed into water containing from 3 to 5 per cent. of hydrochloric acid, which will liberate the sulphurous acid from the bisulphite of soda with which the wool is soaked, and the sulphurous acid being liberated in contact with the fibre, and probably within

the fibre itself, the colouring matter of the wool is acted upon more powerfully by this nascent condition of the bleaching agent than it is by free sulphurous acid. This method resembles the bleaching of cotton by bleaching powder, in the liberation of the bleaching agent by an acid.

Solutions Nos. 1 and 2 rapidly lose strength by the escape of the sulphurous acid, or by its conversion into sulphuric acid by oxidation. Some loss is, therefore, experienced when the bleaching is only required to be done occasionally. The sulphurous acid may be preserved in them to a considerable extent by neutralizing it with carbonate of soda; when required again it can be set free by the addition of hydrochloric acid. No. 3 solution holds its strength much longer than Nos. 1 and 2, and, although it requires a little more labour, the bleaching by it is more effective.

The colour of the wool is often improved by tinting it with a little blue; this may be done in the acid bleaching bath, or, better still, in a bath specially made up for the purpose after the bleaching has been done. I have found a solution of indigo carmine to be best adapted for the tinting, but where the wool is very yellow it is necessary to use a red colour in addition. The colour may be given in the cold.

Bisulphite of soda solution of 45° Tw. is sold at the present time at 9s. per cwt."

After the bleaching has been treated of the lecturer at once enters upon the subject of indigo. He gives an account of its properties and the usual methods of practically or chemically testing its value, and then proceeds to its use in dyeing. There is nothing specially new in the processes given by Mr. Jarman, except, perhaps, with regard to the hydrosulphite process of Schützenberger and Lalande, but it is both interesting and instructive to have a practical and accurate statement of the present methods in use in the woollen dyeing districts, and we, therefore, give it nearly in full. After enumerating seven different kinds of indigo vats, viz., the

copperas vat, woad vat, pastel vat, pastel potash vat, urine vat, German soda vat, and Schützenberger and Lalande's vat Mr. Jarman proceeds :—

“The only vats employed in England for the dyeing of wool, so far as I can learn, are the woad vat, and that of Schützenberger and Lalande. There seems to be a strong objection amongst English dyers to the employment of soda or potash, in consequence of vats being made caustic by the use of these alkaline carbonates along with lime. Caustic potash or soda is exceedingly prejudicial to the soundness and handle of the wool, especially when it is heated along with it; and Schützenberger and Lalande's vat was not at first well received, because soda was used as the solvent of the reduced indigo, and many complaints were made that it rendered the pieces rotten. This is, however, now avoided by the use of lime only as the solvent, too great an excess of lime being carefully avoided.

Utensils.—The indigo mill is a very important apparatus. Unless the indigo is thoroughly ground great loss of that material will take place. Indigo can only be reduced when brought into the condition of an impalpable powder. The mill is either constructed of stones, somewhat like those for grinding corn, and worked by a perpendicular shaft, or it consists of four iron rollers, which are rolled backwards and forwards in a trough by a cradle motion. The indigo is ground with water to a pulp, the operation being continued for several days. The pulp must feel perfectly smooth, and contain no gritty particles.

The vat is a cylindrical iron vessel, having a diameter and depth of 6 feet 6 inches by 6 feet 6 inches to 7 feet 6 inches by 7 feet 6 inches. It is encased by an iron jacket or by brick work, and heated by steam, the steam space in the jacket being about 2 inches wide, and extending from the bottom to within 4 feet of the top. Sometimes the vats are heated by a coil of copper pipe placed inside the vat, which is an economical

arrangement. Direct fire heat is now but seldom employed.

Rakes are used to stir up the contents of the vats. The rake head is about 15 inches long by 5 inches wide, and the handle is 10 or 12 feet long. The rake is lowered down to the bottom of the vat, and a portion of the sediment is drawn up with a jerking motion, when the head approaches the surface. Three or four men work up the vat in this manner vigorously for about ten minutes.

When not in use the vats are covered by a cover, in three pieces, made of battened three-quarter inch boards. This keeps in the heat, and prevents oxidation of the vat liquor to a great extent.

A net of half-inch meshes is lowered down into the vat when wool has to be dyed. The wool is gently moved about in the net by means of a "stang," care being taken that it is not lifted out of the fluid.

When the wool has been in the vat a sufficient length of time, it is lifted out of the net, and placed in a bag made of strong net. The wool is then wrung in the bag, and the liquid returned to the vat.

Pieces, when placed in the vat, are moved about by means of an instrument called a "hawk," one of which is held in each hand, and the piece is pulled towards the operator. It must not be raised above the liquor. In order to prevent the piece from sinking down into the sediment at the bottom of the vat, an iron hoop of the same diameter as the vat, covered with a net having 4 or 5 inch meshes, is lowered down about a yard below the surface of the liquid and suspended there.

A moveable squeezing machine, consisting of two iron rollers 6 inches in diameter, fixed in a frame work, serves the purpose of removing pieces from the vat. One or both rollers may be covered with vulcanized india-rubber.

Materials used in the Woad Vat.—Woad, Madder, Bran, Lime, Indigo.—Woad consists of the fermented

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leaves of the woad plant, *Isatis tinctoria*. This article is grown and manufactured largely in Lincolnshire. The seeds are sown in early spring, and when the plants are large enough they are transplanted in rows. When the plants are from 3 to 6 inches high, the outer leaves are twisted off by children, and then placed under a shed. Usually three crops are thus gathered during the season. The manufacture of the woad is carried on in the winter. The leaves are mixed with lime and urine, and thrown in a heap to ferment. The heap is repeatedly turned over with shovels, to prevent excessive fermentation; this turning of the heap is continued until fermentation ceases. The woad is then packed in barrels and sent to the market. The present price of woad is from £26 to £30 per ton.

Madder contains sugar and nitrogenous matter in addition to its colouring matters. The sugar passes into the butyric fermentation, and furnishes part of the nascent hydrogen; the nitrogenous matter acts as a ferment. The ordinary crop madder is employed. The use of madder in the fermentation vats is not essential, and in many establishments it is not employed. The colouring matter of the madder gives a special shade to the indigo which some manufacturers like.

The bran used is the ordinary bran obtained in grinding wheat. It contains nitrogenous matters and starch; the former assists as a ferment, and the latter passes during the fermentation through the various stages of glucose, lactic acid, and butyric acid, nascent hydrogen being produced at the latter stage.

Newly burnt lime, slaked and riddled, is thrown into the vat in the powdering condition. Its employment serves the purpose of neutralizing the butyric acid as fast as it is formed. When the addition of lime is neglected too long, the butyric acid and other matters pass into the putrid fermentation, which acts destructively upon the indigo.

The indigos found to be the most economical and

effective for woollen dyeing, are the medium qualities of Bengal, ranging, at the present time, from 4s. to 5s. per lb. The violet copper-coloured varieties, having a low specific gravity, are preferred.

Preliminary Operations.—When the indigo-dyed goods are required to have a special “bloom,” the wool or woollen fabric has a “bottom” put on it. Camwood, barwood, Saunders'-wood, cudbear, archil, or archil paste, are the colouring matters which are employed for this purpose. Camwood is the best for wool. The woods give a much more permanent bloom than the weed colours, cudbear and archil, which are somewhat fugitive.

The goods are boiled with the colour for an hour or an hour and a-half, no mordant being used. The quantity of ware is varied according to the depth of shade of bottom required. 16 lb. of camwood or 12 lb. of cudbear for 100 lb. of wool are good proportions for a full bottom.

Of course the blooming is not the only object which the dyer has in view ; economy of indigo is an important matter to him.

It is important that the goods to be dyed should be thoroughly cleansed from all dirt, grease, and soap, or otherwise the dye will be taken up unequally.

Setting the Woad Vat.—The following is the method adopted in the woollen districts of the West Riding:—

Dimensions of Vat, 7 feet diameter by 7 feet deep.—Materials.

	£	s.	d.
5 cwt. Lincolnshire madder* at 26s.	6	10	0
3 pails of bran, weight 18 lbs.	0	1	1
22 lb. slaked lime in dry powder	0	0	2½
2½ lb. madder	0	0	10½
24 lb. of indigo, at 5s.	6	0	0
	£12 12 2		

*Madder in the original ; this may be either a local name for woad or a misprint.—*Ed.*

The woad is chopped and pounded with a spade until the pieces are no larger than a hen's egg. It is thrown into the vat, which is then nearly filled with water. The contents are now heated by turning on the steam, until a temperature of 140° to 150° F. is obtained. The vat is stirred up three or four times at intervals of 15 minutes, and then left overnight. The woad will now be soft and pulpy. Next morning put in the bran, madder, indigo reduced to a smooth paste by grinding, and half the lime, rake up, cover over, and leave till next morning. If the fermentation has commenced, the vat will present the following appearances. A slight froth will rise to the surface when the bottom is slightly stirred with one rake. The liquid, when stirred, will appear green yellow with blue veins or streaks, the green colour predominating. A coppery blue scum called 'flurry' will appear on the surface of the vat. A portion of the bottom drawn up with a rake will show signs of fermentation, and will smell slightly sour. A piece of wool put into the liquid for a short time will be dyed. If these appearances present themselves the vat is progressing favourably, and about a quart more lime may be added, and the whole well raked up. If no signs of fermentation appear, more time must be given before adding the lime, which in this case would only have the effect of retarding the fermentation. If the vat matures satisfactorily, a quart more lime may be added every two or three hours, stirring up well after each addition. The coppery blue flurry will increase in quantity, and the liquid, when stirred, will be green yellow with blue streaks. Then heat up to 140° , cover, and leave overnight. Next morning (the third morning), if the fermentation has proceeded satisfactorily, the vat may be used for dyeing. It is very important that great caution should be exercised in the addition of lime, for if the vat be overdosed fermentation will be arrested, and there will be considerable difficulty in re-establishing it. The vat will then have to be left probably for several days before the fermentation

re-appears. On the other hand, if the addition of lime be neglected too long, and the fermentation passes to the putrid stage unchecked, the indigo will be lost, or, as the dyers say, it will "run away." The liquid exhales an agreeable odour when the progress of the setting is proceeding satisfactorily, but the odour changes when too much or too little lime is present. Much depends on the care and skill of the dyer, for no description of the process can accurately convey to the mind of the uninitiated the mode to be adopted, in the varying conditions to which the fermenting indigo vat is subject. An experienced indigo dyer can exercise perfect control over the condition of his vat.

The following account of the setting of two indigo vats last week, of which I took notes, may be useful.

The vats were intended for the dyeing of broad cloths and wool of a full blue.

Dimensions of vats 6 feet 6 inches by 6 feet 6 inches.— On Wednesday at noon the vats were filled with water, and $4\frac{1}{2}$ cwt. of crushed woad were put into each vat; the liquid was heated to 140° F., and stirred up once. On Thursday morning they were heated up again to 140° and kept at that temperature all day. During the day they were raked up vigorously by four men four times. At five o'clock p.m., 25 lb. of indigo, well ground to a smooth paste, 14 lb. madder, 5 quarts of lime, and 4 pails of bran (2 gallons each), were added, and the whole well stirred up and left overnight. On Friday morning at nine o'clock a light froth rose on the surface when the vat was gently stirred up with one rake. The bottom was in a slight state of ferment and smelt rather sour. The liquid appeared green yellow on the surface with blue streaks when it was stirred by the hand. One quart of lime was added to each vat, and the contents well stirred up for ten minutes as before. It was then covered up. At 11 a.m. and at 1 p.m. another quart of lime was given, and the contents raked up as before. A considerable quantity of coppery blue flurry had now

accumulated on the surface, and the liquid appeared of a dark greenish yellow with blue streaks when disturbed by the hand. The odour was favourable and the fermentation steady, being kept under by the lime. At 3 p.m. the vats were warmed to 135° and another quart of lime added and again well stirred up, appearances and odour favourable as before. At 5-30 the vats were in a condition fit to use for dyeing. Three pints of lime were given to each vat and 5 lb. more indigo; they were well stirred up; temperature 130° . They were covered up and left overnight. At 9 a.m. on Saturday two 60 yard pieces of narrow doeskins were put into each vat, and after they had been worked for one and a quarter hours I took off a sample and left them.

The Dyeing Operations.—Pieces to be dyed a full blue are hawked in a strong vat from twenty minutes to two hours, according to the class of goods, heavy and closely woven fabric requiring more time for the colour to penetrate into the centre than lighter and more open goods. The material is then drawn out of the vat, and after exposure to the air for some time, in order that the reduced indigo may become oxidized and pass into the blue and insoluble condition, the goods are passed into a weaker bath, to dye up to the shade required. For light blue colours, such as are given for wadding for blacks, a single working through a moderately weak bath for about twenty minutes will be sufficient.

For dyeing wool, a vat which shews the fermentation to be in a moderately active state is found to be the best, but pieces are dyed more perfectly in a vat in which the fermentation is kept under.

When the goods are withdrawn from the vat, they are of a fine green colour which rapidly passes to blue. The green colour is due to the instant oxidation of a portion of the yellow coloured reduced indigo, which thus produces a mixture of blue and yellow.

For keeping up the strength of the vat, about 15 lb. of indigo are added every other day, more lime and bran

being added every day. After finishing the day's working of the vats the necessary addition of bran, lime, and indigo is made, and the vats well raked up and heated up to 140° F.

The following table gives the quantities and cost of materials used in a large dye-house for the woad vat for dyeing dark indigo blues on cloth:—

	£	s.	d.
6,533 lb. indigo, at 5s. 6d. per lb. ...	1,796	11	6
68 cwt. lime, at 1s. per cwt.	3	8	0
19¾ packs bran, at 14s. 6d.	14	6	4
142½ lb. madder, at 4¼d.	2	10	6
56½ cwt. woad, at 3os.	84	15	0
12 cwt. fuller's earth	1	16	0
	£1,903	7	4

Per-centage of total cost:—

Indigo	94'37
Fuller's earth	'10
Woad	4'45
Madder	'13
Bran	'76
Lime	'18

99'99

Cloth dyed with the above materials, 159,180 lb. Cost per pound, 3'67 pence.

It is noteworthy that the materials required to reduce the indigo only cost 5'52 per cent. of the whole.

Schützenberger and Lalande Vat.—This vat stands in marked contrast to the woad vat already described, as regards time and the number of vats required. The reduction of the indigo is almost instantaneous; in fact, the reduced indigo may be prepared beforehand, and then it is only necessary to add it to the vat, and proceed with the dyeing in the manner already described. The reduction is performed in the following manner:—

Materials required.—Bisulphite of soda, at 45° Tw., costing 9s. per cwt. Zinc dust, at 23s. per cwt. Slaked

lime in powder, sifted, or in the form of cream of lime. Indigo, ground in water, in the form of pulpy paste, without any gritty particles.

Utensils for the preparation of the reduced Indigo.—

A small tub, or pail, in which to prepare the hydrosulphite. A cask in which the indigo is reduced. Barrels in which to store the reduced indigo. The same vats and utensils which are employed with the woad vat.

To prepare the reduced indigo proceed as follows :—

Pour bisulphite of soda solution into a pail or small tub, and add zinc dust until the smell of sulphurous acid disappears, stirring up well until this takes place. The zinc dust required will be from one-fifteenth to one-tenth of the weight of the bisulphite of soda. The solution so produced is called hydrosulphite.

Place your indigo paste in a cask or tub; add a little cream of lime, and heat to 120° F. Run in sufficient hydrosulphite to reduce the indigo, which may be known when the surface of the mixture assumes a dark green appearance; then add more cream of lime to dissolve the reduced indigo, when the mixture then becomes yellow. It may be known when sufficient lime has been added by taking out the stirring rod, which will quickly assume a bronzed, coppery appearance. If too much lime has been added, the indigo becomes brown, and is partly destroyed, a smell of ammonia being given off.

The creamy fluid is then run into barrels for use.

The Dyeing Operations.—The vat is filled up with water, which is heated up to from 130° to 140° F., and the necessary quantity of reduced indigo run in from the store casks. The dyeing may be carried out exactly on the same plan as with the woad vat; the vat may, however, be used continuously, as it may be fortified at any moment by the addition of reduced indigo. If the indigo in the vat should become oxidized by exposure to the air, and by the air which the goods carry in with them mechanically, it may be reduced by adding hydrosulphite, and also lime if necessary, to the vat. As there

is not such an accumulation of solid matter at the bottom of the vat as there is in the woad vat, vessels having a much less depth may be employed.

The dyer very quickly learns how to manage this vat. The operations are simple and perfectly under control, and they do not, therefore, require an apprenticeship to learn how to manage them, as is the case with the fermentation process.

Opinions of Dyers on the Hydrosulphite Vat.—Since the year 1873, when it began to be used in Yorkshire, the experiences of woollen dyers with this vat have been very varied. It has been abandoned by some and continued by others.

The advantages claimed for it are—that it is easy to manage; that it dyes worsted goods clean; that it can be used either for light or dark blues; that the services of an experienced blue dyer at high wages can be dispensed with; that it is rapid.

The disadvantages attributed to it by those who have abandoned it are—that it is much more expensive than the woad vat on account of loss of indigo in washing; that the goods handle thinner when of the same weight and texture, although the strength of the goods is not impaired, as tested by Hebden's machine; that the colour is not quite so good, being somewhat green; that it requires one-third more red bottom than the woad vat; that it spoils the face of goods.

The heaviest charge against it, however, seems to be the cost, but this may be very greatly lessened by recovering the indigo which washes off by passing the goods through milk of lime before the washing. The lime dissolves the reduced indigo which has not become fixed to the fibre. The green colour can be removed by passing the goods through very dilute sulphuric acid in the washing machine.

The following table gives the cost of dyeing dark blues by the hydrosulphite vat, by a dyer who wished to use it, but was deterred by the cost. It bears unfavourable

comparison with the cost of materials by the woad vat. The cost of labour in working the two vats may be assumed to be about the same :—

	£	s.	d.
240 lb. indigo at 5s. 6d.	66	0	0
1,978 lb. bisulphite of soda at 1d. ...	8	4	10
195 lb. zinc dust at 23s. per cwt....	2	0	1
30 lb. fuller's earth	0	1	0
lime	not given.		
	£76	5	11

Per-centages of total cost :—

Indigo.....	86·84
Bisulphite soda.....	10·62
Zinc dust.....	2·61
Fuller's earth.....	nil.
Lime.....	not given.

100·09

Cloth dyed with above materials, 3,420 lbs. Cost per lb., 5¾d.

The materials required to reduce the indigo cost 13·25 per cent. of the whole."

The lecturer concludes the second lecture by treating of sulphate of indigo, and the colours which may be obtained from it.

The third lecture commences with general remarks upon colour, fast and loose colours, and fixation of mordants and lakes. We pass on to the practical instructions concerning mordanting.

"Modes of Applying Mordants on Wool.—In wool-dyeing the goods are always mordanted at a boiling temperature.

Boiling seems to have the effect of opening the pores of the wool and expelling the air, thus giving passage to the mordant solution.

The mordant may be either applied before the dyeing operation, along with the colouring matter, or after the

dye has been applied. Sometimes it is found advantageous to apply the mordant both before and along with the dye.

The application of too much mordant is to be avoided ; this is notably the case with the iron and bichrome mordants, which produce rusty and green shades respectively, when an excess of the mordant has been used.

Utensils Employed in Mordanting.—The most convenient vessels for mordanting woollen goods are wood cisterns, 6 to 8 feet long, 4 to 5 feet broad, and 3 to 4 feet deep, with a false bottom made of perforated iron plates. The water is heated by a perforated steam-pipe, 2 inches in diameter, which passes under the plates along the middle of the cistern. When scarlets, oranges, and crimsons have to be dyed with an acid tin mordant, block tin plates should be substituted for the iron plates, which would seriously affect the colours, as iron salts would be formed by the acid acting upon the iron plates. Metallic iron also decomposes tin salts, the tin being precipitated in the metallic state. Large iron pans are also frequently used in both mordanting and dyeing, the water being heated, either by a steam-pipe blowing straight down into the water, or by direct fire-heat under the pan. The steam in this case is only employed to heat up the water to the boil, the subsequent mordanting or dyeing being done by the fire-heat alone. Many experienced dyers prefer direct fire-heat, especially for the dyeing, as a temperature can be obtained which is two or three degrees higher than what can be obtained by steam alone; and fire-heat is more especially preferred for wool, which is kept in a more constant state of agitation by the ebullition of the water than can be obtained by steam-heat. The wool is also less liable to be felted or twisted into tails.

A more uniform ebullition and agitation of the liquor may, however, be obtained by passing the steam-pipe, not perforated, several times along the bottom of the cistern, and allowing the condensed steam to discharge

itself into the cistern by an upright pipe, bent over above the surface of the liquid. When the steam pressure is not less than 50 lb. per square inch, this is an excellent and economical mode of heating both the mordant and dye baths.

When pieces are mordanted or dyed, they are kept in motion by causing them to pass over a wince, placed over the dye vessel and turned by machinery. Three or four pieces are sewed end to end, and are thus passed over the wince continuously.

Wool is kept in motion by being stirred up almost continuously during the process by long poles, called "stangs." The thorough stirring and breaking up at the commencement is of great importance, in order to prevent unequal reception of both mordant and dye.

The mordanting usually occupies from one to two hours, the liquor is then run off from the wool, and water run in once or twice to wash out excess of mordant, it is then put in a coach or waggon, covered over with a sheet, and left over-night, or longer if convenient. The colour obtained after leaving it in this manner is always better than when it is passed direct into the dye-bath after mordanting.

Pieces after mordanting are drawn out of the bath, washed in the washing machine, and left over-night before dyeing."

Upon the use of tartar or argol with copperas we have the following:—

"Tartar or argol is almost invariably used along with the copperas, in order that the solution may be kept clear, and the too rapid dissociation of the copperas prevented. The tartar, in this and every case where it is used with a mordant for a similar purpose, should be added to the bath first, for it is easier to prevent a precipitation than to redissolve the precipitate after it has formed. Copperas is frequently used simply as a saddener; its effect upon colours is to produce dark shades. It is used both alone and in conjunction with alum and sulphate of copper, but

not with bichromate of potash, which it reduces and renders its special properties less effective as a mordant."

Upon the use of bichromate of potash in wool dyeing, the lecturer says:—

"This splendid salt is met with in commerce in a state of almost absolute chemical purity. I think it is more extensively used in our woollen dyeing than any other mordant. Its decomposition in the bath in contact with wool is different from that of any other mordant, for its constitution is different. The metal which is deposited as a hydrate upon the wool, is present in this salt as the acid, and not as the base, which is potash. Bichromate of potash may be represented as being neutral yellow chromate of potash, in combination with dry chromic acid. To obtain the full effect of the bichromate as a mordant, sulphuric acid is usually employed along with it; the whole or major part of the chromic acid is thus set free. Chromic acid is a most powerful oxidizer, and acts energetically upon wool, and should, therefore, be used with caution, as we shall see further on. The wool furnishes the reducing agent, probably in the form of hydrogen, which acts upon the chromic acid. The chromic hydrate thus produced is deposited upon the wool as the mordant hydrate, a portion of neutral chromate of potash is also usually present on the fibre.

I have ascertained experimentally that it is not safe to use more than 3 per cent. of the weight of wool of bichromate, for if 4 per cent. be used the colour becomes impaired, and if 12 per cent. be used the wool cannot be dyed with logwood at all, and the curious effects of over-chroming are produced. These effects are due to the destructive oxidizing action of the chromic acid upon the wool. When a still larger quantity of bichrome is used along with sulphuric acid the wool is dissolved, and a solution of chrome alum is obtained."

Some remarks upon tin solutions close the third lecture. We hope in our next to be able to give some further extracts from Mr. Jarman's lectures.

2. *Critical and Historical Notes concerning the Production of Adrianople or Turkey Red, and the Theory of this Colour.**

BY THEODORE CHATEAU.

Corresponding Member of the Industrial Societies of Mulhouse and Amiens, etc., etc.

Theory of M. Fenny.—In 1869, M. Jenny presented a memoir upon the Theory of the Turkey red process to the Industrial Society of Mulhouse. It was the subject of a report by M. Schaeffer, which was not altogether favourable. However that may be, we shall see that the work of M. Jenny is that of a well-informed practical chemist.

Concerning the scouring he says: The first operation to which the cloth is subjected has for aim the removal of certain impurities acquired in the course of spinning and weaving. The process consists in a maceration in warm water; the saline matters are dissolved, and the starchy matters transformed into glucose by the fermentation which is quickly set up in the mass, especially when the germs which exist on the grey cloth have not been destroyed by the heat of singeing.

After the starchy matters of the size have been removed, the cloth is passed into a boiling alkaline solution to remove fatty and resinous matters. The use of lime and rosin soap as commonly employed in bleaching ought not to be allowed in bleaching for Turkey red dyeing.

Oiling.—For this operation a mixture of alkaline carbonates, cow dung, and emulsive oil is employed.

Carbonate of potash is to be preferred to carbonate of soda in warm and dry climates on account of its hygroscopic nature, which is advantageous in the process. In most climates, as in England, carbonate of soda is used. For general use it would seem that a mixture of the two salts would be preferable.

The cow dung, no doubt, acts in two ways: the nitro-

* Abstracted and condensed from the "Moniteur Scientifique," vi. (3) p. 1012.
Concluded from vol. ii., p. 200, Textile Colourist.

genous mucilaginous matter which it contains (bubulin of M. Morin) swells up considerably in alkaline carbonates, and assists in forming an emulsion with the oil; on the other hand, the putrefaction of the dung leads to the formation of carbonic acid, the utility of which will be shewn later on.

The oil exclusively employed in our country (France) is olive oil; it should be emulsive, that is, in contact with alkaline solutions it ought to produce a persistent emulsion or milkiness; this property is owing to the presence in the oil of a larger or smaller proportion of fatty acids, which form a jelly with the alkalies, the thickness of which maintains the fine particles of oil in a state of suspension.

All the processes for making oil emulsive, have for aim the splitting up of the glycerides and setting the fatty acids at liberty. Margaric acid is very easily made into an emulsion, even with carbonate of potash at $1\frac{1}{2}^{\circ}$ Tw.; it should therefore be considered as more useful in an oil than oleic acid. The emulsive state of the oil allows it to be diffused in a very uniform manner through the fibre.

The oiled goods are hung up in the air to dry. This drying should be at a low temperature. It is for the purpose of removing the water, which, if not removed, would cause the oil to separate superficially, and to be detached in the succeeding operations. In this operation the carbonates are changed into bicarbonates, the carbonic acid being partly derived from the air and partly from the putrefaction of the cow dung.

The hot stove drying which follows has for action the freeing of the oil from its emulsive envelope (a tissue of fatty acids, soap, and mucilage) and allowing it to penetrate to the fibre and gradually impregnate it; it is important that this liberation of the oil should take place slowly and progressively. The following facts are to be kept in mind: the separation of the oil takes place because the gelatinous envelope formed by the fatty acids and the alkaline carbonates, under the influence of an increased temperature, become sufficiently fluid to permit the oil globules to come to the surface and separate. The oil thus separated is not capable

of forming an emulsion, it no longer contains free fatty acids.

The carbonic acid gas liberated in traversing the emulsion, helps the separation of the oil; as it cannot act until the alkalies are saturated, it is evident that the separation will be more rapid with weak liquors than with strong ones.

The quantity of oil separated is greater with strong liquors than with weak ones, at a higher temperature than at a lower one, after twelve hours than in shorter periods, with caustic than with carbonated alkalies, with potash than with soda. The soap which is formed plays an important part in the separation of the oil on account of its great emulsive power.

The following oil baths continue the action, they should be repeated until the fatty acids have been completely saponified, and until all the oil has penetrated the fibre, and the excess of soap removed.

Several chemists have expressed the opinion that the oil does not take any part in the dyeing until it is oxidized upon the surface of the fibre, and this oxidized oil, under special circumstances, possesses the properties of, and acts as a mordant. M. Jenny disputes this view, for he has satisfied himself by direct experiment that only a very small portion of the oil is oxidized, and is quite insufficient to have any important action.

If, then, all that is required is to deposit a certain quantity of oil upon the surface of the cloth, would it not be possible to operate by quicker and cheaper methods? The necessity of employing alkaline carbonates has been always admitted; these salts act upon the fibre in a physical manner, and render it more capable of combining with colouring matters.

Mordanting.—Neutral solutions of alumina salts are decomposed by contact with the fibre; there is dialysis; the alumina is precipitated on the surface of the cloth, the oil opposing its penetration into the fibre; the soap which remains, even after numerous washings, produces oleate of alumina. Tannin and phosphates help in the decomposition of the alum.

Dyeing.—Alizarine and purpurine have an equal value in

Turkey red dyeing, but the purpurine being more soluble than the alizarine fixes rapidly, while the alizarine only acts through the presence of tannin, which is an excellent solvent of this colouring matter.

The blood which is frequently added in the dyeing removes, by means of its albumen, the brown and resinous matters which would tarnish the colour. The chalk is simply useful by neutralizing the acids contained in the madder. The alumina and oleate of alumina become saturated with colouring matter. The dye is at its maximum of depth and brightness at from 122° to 140° F., as the absorptive power of the alumina becomes weaker at higher temperatures; but it is necessary to carry up the temperature to ebullition, in order to convert the alumina into meta-alumina, which resists more perfectly the action of the fatty matters used in soaping and brightening.

Brightening.—The aim of this process is to remove from the lake all foreign matters, to saponify a notable quantity of the oil, and to remove from the cloth the greasy feel which it has up to this point; to reduce, by means of the tin salt, the brown matters which become soluble and are removed, and to replace part of the alumina by oxide of tin.

During the brightening the alizarine is set at liberty. It dissolves in the oil which adheres to the cloth, which thus, becoming saturated with colour, adds its effect to that of the lake.

Conclusion.—There remains upon the tissue a compound of fatty acids, alumina, lime, oxide of tin, purpurine, and alizarine. This compound is penetrated and protected by an oil perfectly neutral, and saturated with pure alizarine. The lake is deposited in such a manner in the fibre that it presents to the eye all the brilliancy and fire which it is possible to give it.

Wartha's Opinion.—M. Wartha, after his researches upon Turkey red, states that the particular lustre of the Turkey red is due to a peculiar combination of fatty acid with alizarine; a combination which does not adhere very strongly to the fibre, and which can be dissolved by the petroleum oils and ether. If the solution in petroleum or ether be evaporated, a

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fatty matter is obtained of a bright scarlet red colour, which can only be decomposed by the action of very strong potash, and then it presents the characteristic reactions of alizarine. The extracted matter loses all its brightness, and acquires a cherry red colour, exactly resembling madder colours produced by simple mordants of tin. (?)

Muller's Experiments.—M. A. Muller continued and extended some of the experiments of M. Wartha. He was impressed with the difference of time required by the petroleum or ether to dissolve the colour from samples of Turkey red cloth obtained from different establishments. An attentive examination pointed to an interesting and unexpected fact, which was, that the time required to remove the colour was not at all influenced by the variable quantity of alizarine, but was in direct proportion to the fastness of the colour as tested by ordinary means, and that this power of resistance was undoubtedly owing to the method of mordanting. M. Muller found, by continuing his experiments, that the greater the amount of alumina in the colour the longer it resisted the bleaching action of a mixture of alcohol and hydrochloric acid; and, reciprocally, those cloths which yielded most colour to ether (the combination of alizarine and fatty matter) were most quickly bleached, and were, in every respect, less fast.

M. Muller does not mean to intimate that the use of a large quantity of oil in any way affects the fastness of the colour; but he believes that his experiments demonstrate that only that portion of the oil which has undergone the unknown modification in which it is insoluble in ether, commonly called oxidation, contributes to the Turkey red colour; and further, that it is very possible that an excess of fatty acids, not saponified, may, under the influence of light, act very injuriously upon the alizarine.

To support this, M. Muller quotes some experiments made by taking equal weights of dyed cloth, or of yarn of the same counts, or stripes of the same dimensions, which were placed in the decolourizing solution composed of 10 measures of alcohol at 96° and 1 volume of hydrochloric acid, sp.

gr. 1.18. The mixture, which must be used in rather large proportion, is slowly warmed on a water-bath to 122° F. The various samples are seen to gradually yield to the action of the fluid, first one and then the other becoming white. The time which is required for the red to disappear being noted, numbers were obtained which agreed sufficiently well with the known goodness of the colours.

M. Chateau then gives a *resumé* of the various theories which have been detailed in this long memoir; we omit it as unnecessary, and pass on to his own summing up of the subject.

If the various theories be well considered it will be seen that they take three different ways, which, however, have more than one point of contact.

One set dwell upon the animalization of the cotton.

Another upon the oxidation of the oil, to which is attached, chemically speaking, the idea of the action of the fatty acids and especially the oleic acid.

A third set consist of those which compare Turkey red dyeing to the operations of tanning, and have a certain relation to the animalization theory.

As different in details as the various systems recounted are, the nature of the substances employed, and the manner in which they are employed has considerable resemblance.

The substances used may be grouped as follows:—

- (1) The fatty matter, vegetable or animal.
- (2) The albuminous matters, vegetable or animal, in natural or artificial solution or in suspension in oils, alkaline emulsions, etc. Examples: natural emulsive oils, yolk of egg, blood, ox gall, excremental matters of herbivorous animals, etc.
- (3) Tannin matters, as cadou, myrobalans, fustic, gall-nuts, sumac, etc.
- (4) Aluminous matters, as alum and other salts of alumina, aluminous earths, etc.
- (5) The colouring principles of madder or other similar exotics, and, at present, artificial alizarine and purpurine.

(6) The brightening or clearing matters, such as the oxygen of the air, alkaline carbonates, bran, tin-salts, etc.

The sequence of operations is also sensibly similar. After having prepared the cotton by bleaching, the next step is to steep the goods in an alkaline oily emulsion containing always an albuminous substance or an albumenoid material, and drying after each time at a determined temperature,* afterwards the galling and aluming takes place, that is, the alumina and tannin are introduced; next, the dyeing; and, lastly, the brightening, which in India is accomplished by exposure to sun and air, and in Europe by means of soap, bran, or tin-salts.

In proportion as chemical knowledge advances we perceive the number and duration of the operations diminish. In India the process requires three months; in Europe it has been reduced in the case of M. Cordier's process to five or six days for either cloth or yarn.

The analysis of Turkey red cloth and the oiled cloth shews the same principles more or less modified by the various physical and chemical agents to which they have been subjected. The following substances are found:—

(1) A fatty matter, called modified, that is a fatty acid simple or compound.

(2) An albumenoid matter (albumen, mucilage, caseine, or protein matter).

(3) Alumina.

(4) Tannin or a similar substance, or in a modified state.

(5) Colouring matter, principally alizarine and purpurine. We say principally alizarine and purpurine because in certain specimens of Turkey red there may be discovered other colouring matters which have been used to serve, as it is said, for a bottom, applied either before or at the same time as the madder. It must be noticed also that in certain Turkey reds

* It is worthy of remark, that, in the drying after each oiling, the temperature does not pass the point at which the albumen coagulates. The drying is accomplished without the albumenoid being coagulated, which only takes place at a later stage.

there is no tannin matter, this material not being absolutely essential to the colour.

If the various processes be studied in a theoretical point of view and the expressed theories themselves be considered, we observe one fact in particular, and that is, that nearly all the theories attribute an important part to the albumenoid principles, and we do not think that the theory of modified oil is in opposition to this. In the experiments of Chevreul, Weissgerber, and Schützenberger upon the peculiar fatty matter extracted from dyed or oiled cotton, we remark that these chemists describe it as a very complex substance in which fatty acids predominate. The examination of this matter has been left incomplete, and there is nothing to contradict the assumption that it may contain some albumenoid substance, or may contain also oleate of alumina combined with a protein matter so mixed or combined as to be soluble or extractable by the essence of turpentine, acetone, or alcohol used.

In every chemical theory the practical operations employed should be considered, and the use of either vegetable or animal albumenoid substances is so general in nearly all the Turkey red processes that it cannot be overlooked. Many dyers have their particular secrets or methods of working, but most of them agree in stating that the utility of an animal albumenoid matter is beyond doubt, whether this matter be derived from the excrements of herbivorous animals, or internal secretions of the animal, as blood or gall, or whether it be obtained from other animal matters, as gelatine, fibrine, or similar substances, the logical deduction of which leads to the idea of the animalization of the vegetable fibre; and we repeat that this idea is not in opposition to the theory of an oxidized oil or fatty acids, for it can be easily conceived that the animal matters might contract a combination with the so-called modified oil or with the fatty acids resulting from the oxidation of the fatty matter, for such combinations do exist in cerebral substances, bilious substances, and yolk of egg.

This hypothesis seems admissible from facts which we

know in connection with the subject, which are chiefly that fatty acids are naturally contained in or are purposely added to the oils employed ; that either a vegetable albumenoid matter (mucilage of the oil), or an animal albumenoid (blood, gall, or excrements) are in use ; that the colouring matters of madder (alizarine and purpurine) are soluble in oils and fatty acids, oleic acid among others, and that these colouring matters are not only soluble in albuminous solutions, but, as Berzelius has shewn, they contract an intimate combination with albumen. To these considerations we may add, that the state of hydration of either alumina or albumen has much influence upon dyeing in general, and Turkey red dyeing in particular. For recently precipitated hydrated alumina takes only a pink colour, while if dried (not ignited) so as to obtain an impalpable powder it takes a red colour of a much higher tone ; the alumina in the latter state being still hydrated ; the dyeing in both cases having been made with an alcoholic solution of madder. In the same manner colourless albumen recently coagulated takes only a pale colour, but if carefully dried and reduced to fine powder it acquires a dark red colour. The contrast is more striking in the case of albumen than in alumina. The same differences have been observed under various experimental modifications.

In considering the experiments of Vogler and others, where the fatty matter is omitted, we were led to experiments which assured us that it is possible to produce alumino-organic lakes upon the fibre without any fatty matter, which have much resemblance in tone and hue to Turkey red ; for example, a triple insoluble combination of albumen, alumina, and tannin can be produced by taking a solution of egg or blood albumen, adding acetate of alumina (the liquor remains clear), and then a water solution of tannic acid ; a white precipitate is produced, which, when collected and dried by a gentle heat, has a strong attraction for the colouring matter of madder, producing a dark red colour. The same experiment made upon cloth under the conditions of practical dyeing gave the same result.

In this combination the tannin appears useful, for the

precipitate obtained by coagulating a mixture of alumina salt and albumen by heat or by alcohol gives a yellower colour; the action of the tannin appearing to be to attract the red colouring matter, a fact which had been previously noticed by others.

To the above combination lime may be added; to a solution of albumen a solution of alum is added, then lime-water and an aqueous solution of tannin. There is an immediate coagulation; heat to collect the precipitate, which may be washed with hot water. Although the alum was used in excess the precipitate only shewed upon analysis 2.5 per cent. of alumina, the wash water did not shew either lime or tannin present. This precipitate, dried and powdered, dyed up also a dark red in either alcoholic or water solution of madder, or garancine. As in the first case this quadruple compound can be produced upon cloth.

In both cases the coloured lakes withstood the brightening action of bran, soap, and salts of tin.

To resume, an attentive study of the various methods of dyeing and the observations which we have made and gathered, lead to the following conclusions:—

(1) That the fatty matter employed carries with it a fatty acid, oleic acid, or gives birth to a fatty acid, the same or a similar fatty acid, or a mixture of fatty acids in which oleic acid predominates.

(2) That in the aluming this fatty acid, simple or compound, combines with a certain quantity of alumina set at liberty, forming a fatty salt of alumina, which may also be formed by means of double decomposition between alkaline fatty salts and alumina salts.

(3) That this fatty acid contracts at the same time a species of combination with the albumenoid matter, either with the vegetable albumen of the emulsive oils, or with the animal albumenoids of yolk of egg, blood, or galls when these substances are used, which is very frequent, or with the albumenoid matters of the cow dung, sheep dung, etc.

(4) That this triple combination of fatty acid, alumina, and

albumenoid matter does not possess the stability of a definite compound, and that it is split up by the action of neutral solvents, such as essence of turpentine, acetone, petroleum spirit, bisulphide of carbon, alcohol, etc., and becomes separated into various parts, some soluble in these fluids, others insoluble and remaining thick.

(5) That this triple combination does not contract an intimate union with the fibre, since the solvents above named remove it from the tissue, upon which it is only superficially placed or not deeply seated; a fact which may constitute one of the physical characters to which the brilliancy of Turkey red is owing.

(6) That this triple combination unites or dyes by contact with colouring matters, without forming an intimate combination with the fibre of the cotton, such as takes place in the dyeing of ordinary mordants.

(7) That the lake thus formed and separated from the fibre, or produced independent of the fibre, is capable of being brightened by the ordinary methods.

(8) That the state of hydration, or rather dessication, of this triple compound of fatty acids, alumina, and albumenoid matter has an influence upon the tone of colour.

(9) When galling forms a part of the process (which is not always the case), the tannin probably precipitates the alumina from the alum, and at the same time attracts the chief colouring matters of the madder, and gives a greater stability to the above quadruple combination.

It will be seen that we are in favour of the theory of animalization, but we wish that the sense in which we use the word should be clearly understood.

We do not mean, as was formerly supposed to be the case, that the fibre itself undergoes a change, and acquires some of the properties of wool or silk. By animalization we mean the deposition upon the surface of the fibre, or to some small depth within it, of an animal organic mordant, which is supported by the vegetable fibre, and permits it in dyeing to be covered with a uniform colour.

3. Upon the "Greening" of Aniline Black.*

I OBSERVED also, that the muriate of aniline blacks at 42 and at 63 of aniline per 1,000 of colour, shewed no difference in the ease and quickness of their turning green.

Another black, that containing a mixture of salt of naphthylamine resists pretty well, but it is not the black which resists, it is a brown which forms at the same time ; in other respects this black, having but little brilliancy, would not be readily employed.

In the ageing trials the best blacks were those which had been aged at the highest temperature.

As to the methods of raising or washing off, the most intense blacks (without considering the whites) were those passed in bichromate of potash alone, then come those passed in silicate, chrome, bleaching powder and soap ; and, lastly, those passed in solution of crystals of soda.

As to the action of sulphurous acid, the black raised in chrome alone resisted the best ; but this was apparently owing to a mechanical effect of some thickening remaining, for the same blacks, when chlored and soaped, did not resist. It was not, therefore, a character of the black itself, but a protecting power of the thickening.

It follows, therefore, that I have not been able to obtain a *practical black* which could resist the influences which turn the black green. I had hoped by precipitating the black in various ways and fixing the precipitate, to obtain a less sensitive black. I reckoned upon the mechanical action of the fixing agent envelopping the finely divided particles of the precipitate, and obstructing the entrance of the greening gases. With the same idea, I tried, besides albumen and casein, silica, wax, calcareous soaps, lime, and alumina, but all the results were negative.

My opinion is that the greening cannot be completely pre-

*Continued from p. 230.

vented ; there will always be an action, but it will be naturally less appreciable to the eye in a strong black than in a weak one.

M. G. Witz's paper upon this subject is entitled "Upon the Greening of Aniline Black in presence of acid oxidizing agents." He says, the greening of aniline black in presence of acids of the oxidizing class having been found in several cases, I desired to confirm the fact by a series of new experiments, selecting the conditions most favourable for the opposite opinion.

(1) A piece of calico printed with aniline black had the thickening washed out with hot water, and was then placed in a dish with a 5 per cent. solution of chlorate of potash. I then gradually added dilute hydrochloric acid at 3.65 per cent. of acid. Much less than an equivalent of acid changed the aniline black to a bronze-green colour; that is to say, that the presence of a large excess of chlorate did not influence in any sensible degree the action of the hydrochloric acid upon the aniline black.

(2) To ascertain the influence of temperature upon the mixture I heated it to 158° F., after having coloured it with litmus; no change was observed.

Imagining that in certain of the experiments the decomposition of the chloric acid at a high temperature had led to some action due to the chlorine products, I boiled the solution for several minutes; the litmus was completely bleached, but the bronze-green colour remained unchanged even after washing and drying.

This modification of the original experiment appears to me to render untenable the hypothesis of the deoxidation of aniline black by acids, inasmuch as the colouring matter of the litmus was destroyed by an oxidizing agent at the same time that the aniline black became green.

On the other hand, an alkaline solution changes the green-bronze colour to black; the action appears to be a modification of the same kind which alkalies have upon litmus and other colouring matters.

The action above related of hydrochloric acid in presence of chlorates is not new, and is probably as old as aniline black. I mentioned it previously as an answer to opinions expressed in the chemical section of the society; and in order to further prove that the greening of aniline black is not a case of deoxidation, I will give some other illustrations.

(3) By contact with pure diluted nitric acid, both ordinary and chromed aniline black become instantly green in the cold, the same as with hydrochloric acid. The same action takes place with hot acid, and if a little sulphate of indigo be present it is suddenly bleached upon the mixture being heated, and even after the exercise of this oxidizing action the aniline colour remains green.

(4) A crystal of pure nitrate of mercury placed upon a moistened sample of aniline black, whether chromed or not, has a sensible greening action upon it. The nature of this salt prohibits the idea of any deoxidizing action taking place.

It is true that chromic acid alone, or chromic acid dissolved in dilute nitric acid, only acts upon aniline black in so far as to give it a violet shade. Without doubt there is in this case a destructive action on the black, similar to that effected by chlorine or hypochlorous acid, even in presence of other acids. These agents acting upon the black even more powerfully than the acids, which merely green it, has led to a belief that, since the black does not become green during certain oxidizing reactions, its greening is owing to deoxidation.

(5) Diluted sulphuric acid turns the black to a bronze-green. When a sample of aniline black, even when chromed, and whether it has been previously greened by acid or not, is immersed in sulphuric acid at 14° Tw., mixed with a small quantity of a saturated solution of crystallized permanganate of potash, a decolouration is observed to take place in the course of a few minutes, the green being hidden by the brown coloured oxide of manganese, which deposits upon the fibre. Being afterwards treated with an acid, especially oxalic acid, the sample will appear of a fine white if the black has not been very dense. By this treatment the strength of the fibre is not considerably injured.

It is possible to thus remove accidental stains of aniline black from cloth by alternate treatments with solution of permanganate and oxalic acid, either in solution or in fine powder; tartaric acid does not act so well as oxalic. M. J. Depierre has recently shewn that a mixture of bichromate of potash and oxalic acid has a similar action upon aniline black.

(6) I will only recall the fact that I have found the same reaction with pure chloric acid in solution and in the cold. The aniline black first became green and then was bleached.

It is well known that during the ageing of the aniline black colour, and while it is being formed upon the cloth it has invariably a green hue, and does not become black until the acid bodies present are either removed or neutralized.

If it is insisted that hydrochloric acid may become split up into hydrogen and chlorine, and that the hydrogen deoxidizes the black, it may not only be objected that this is a very stable acid, but also asked what then becomes of the chlorine liberated? But as the smallest quantity of litmus present is never bleached, it is evident that there is no production of chlorine, and that therefore there is no deoxidation of the black when in presence of hydrochloric acid.

It is shewn, however, that when a chlorate exists in solution with the hydrochloric acid, the greening takes place the same. In the second phase of this experiment, that is, when by heating, the chloric acid begins to suffer decomposition—as is proved by the bleaching of litmus—the greening of the black is still evident. It is probably only when the chlorine products become abundant that another reaction is observed.

From all these observations it is concluded that the greening of aniline black is due to a special action of acids, and not to deoxidation.

[To be continued.]

4. *Abridgments of Complete Specifications of Patents Recently Published.*

A.D. 1875, November 29th.—No. 4134.

HUMMERSTON, JAMES. "A new or improved Machine for Printing on Paper, Floor-cloths, and Woollen, or other Woven or Felted Fabrics." The object of this invention is described by the patentee as being "to print patterns of any description, or design, or colour, on wall-papers, and to produce an effect equal to hand-stained or printed work; also to print patterns of any description, design, or colour, on floor-cloths, or on woollen or other woven or felted fabrics, saving thereby much time and skilled labour." There are three detailed drawings accompanying the specification, without reference to which the machinery cannot be described, but the following statement will give a general idea of it. "Between suitable framework I fix a table, over which is made to travel a sheet, motion being given thereto from suitable motive power. One or both rollers over which the sheet is made to travel is, or are, made adjustable by suitable regulating screws, in order to give the sheet the required tension. Above the table I mount a beam, the ends of which are fitted to slide freely in bearings on the framework. To the beam is attached a carrier, in which is fixed the block containing the pattern. This block may be of the ordinary construction to that used in ordinary hand printing."

"An intermittent vertical reciprocating motion is given to the beam, to which the carrier is attached by preference through the medium of a cam or heart-motion arrangement; motion being given to the cam or heart arrangement from suitable motive power."

"In order to put the required amount of colouring matter on the block previous to the impression being made, I provide a sliding table, on which is deposited the colouring matter, and spread thereupon by means of rollers in a similar

manner to those used on the ordinary printing or lithographic machines."

"The roller containing the paper, cloth, or other woven or felted fabrics to be operated upon, is mounted in any convenient position in bearings on the framework so as to revolve freely."

"The paper, cloth, or other felted or woven fabric, is drawn from the roller by friction rollers or other convenient arrangement."

"The required reciprocating horizontal motion is given to the sliding table by preference from a cam or heart-motion arrangement, and transmitted thereto through suitable gearing."

"The colouring matter may be fed to the colouring rollers by means of a hopper or other convenient means."

The claim is for "the arrangement, construction, and combination of the various parts forming the machine for printing patterns of any design or colour on wall-papers, floor-cloths, or on woollen or other woven and felted fabrics, and any mere modifications of the same."

A.D. 1875, December 2nd.—No. 4168.

FORD, ALFRED. "Improvements in the Method of Cleansing Wool and of Recovering the Products." (*Provisional protection only.*) "The object of this invention is to obtain from wool, by the act of cleansing, the grease or other matters which it contains in their natural state, unaltered by chemical action." This was to be accomplished by employing spirit or oil of turpentine, rectified by distillation and known as camphine. To keep down evaporation and improve its cleansing powers it was to be mixed with 5 per cent. of heavy oil, mineral was preferred. The wool to be treated was agitated with this mixture until it was cleansed, and then the excess of liquid expressed and used for a fresh parcel of wool until it became saturated. The grease was obtained either by distilling off the camphine or mixing it with water. The wool was to be finally washed in warm water with soap and dried. Besides rectified turpentine other hydrocarbons can be used.

A.D. 1875, December 22nd.—No. 4454.

KEMPE, WILLIAM and KEMPE, ARTHUR. "Improvements in Raising the Nap upon Cloths and Fabrics, and in Apparatus employed therein." This patent is for a substitute for the natural teazel, which is made with a set of needle points, "formed of steel wire sharpened, and brought to a conical point of a similar form to the points of needles." There is a drawing attached to the patent, shewing the arrangement of the needle points for working.

A.D. 1875, December 28th.—No. 4515.

WILDE, HENRY. "Improvements in the Manufacture of Metal Rollers for Printing Calico and other Textile Fabrics, part of which is applicable to the Refining of Copper." This invention is for the depositing of copper by electricity upon rollers made of iron or other metals cheaper than copper. The inventor states that the attempts made in this direction have hitherto proved commercially unsuccessful, "on account of the expense of the battery power, and the slow rate at which the copper was deposited in the reguline state." The novelty of this invention consists "in giving to the electrolyte or depositing liquor, in which the roller to be coated is immersed, or to the positive and negative electrodes themselves a rapid motion of rotation, in order that fresh particles of the electrolyte may be brought successively in contact with the metallic surfaces. By this means powerful currents of electricity may be brought to bear upon small surfaces of metal, without detriment to the quality of the copper deposited, while the rate of the deposit is greatly accelerated.

"The iron roller to be coated with copper is mounted on an axis, the lower end of which is insulated, to prevent its receiving a deposit of copper at the same time as the roller. The roller, after having received a film deposit of copper from an alkaline solution in the manner well understood, is immersed in a vertical position in a sulphate solution of copper, and a motion of rotation is given to the roller or rollers, by means of suitable gearing."

The positive electrodes to keep up the supply of copper are

copper rollers or cylinders, corresponding in length to the iron roller.

"The sulphate solution may be maintained at a uniform density from the top to the bottom of the bath by rotating a small screw propeller enclosed in a tube communicating with the liquid, and driven by the same gearing that imparts motion to the roller."

"The electric current employed is that derived from the electro-magnetic induction machines," for which the inventor holds several patents, "or other machines constructed on the same general principle."

A.D. 1876, January 20th.—No. 238.

LEVINSTEIN, IVAN. "Improvements in the Application and Treatment of Residues arising from the Manufacture of Magenta." (*Provisional protection only.*) This invention consists in treating the residues from the magenta melt by dilute acid, preferably hydrochloric, by means of which a partial solution is obtained, which solution is to be applied for dyeing paper in the ordinary manner; "if the brightest shades are required, I allow the mass to settle and decant the clear liquor for use."

A.D. 1876, January 21st.—No. 250.

MATHER, WILLIAM. "Improvements in Apparatus for Steaming Printed Fabrics." "This invention relates to certain improvements in the apparatus for which letters patent were granted to me in conjunction with Honoré François Adolphe Cordillot, on the 9th day of February, 1875, No. 479.*

"In the specification of the said patent the apparatus described consists of a closed chamber with a door at each end, and with a series of waggons to receive the fabrics, the said waggons running on rails on the floor of the closed steaming chamber, and being discharged at intervals when the process is completed. Now my invention consists in dispensing with the waggons and their accessories above referred to, and making the supply and discharge of the fabrics continuous and self-acting. To accomplish this the

* See Textile Colourist, vol. i., pp. 50, 106 and plate.

pieces of fabric are piled on to a "creeper," which may be formed either of an endless belt of blanket or other suitable material or by placing a series of metal or wood rollers almost touching each other along the bottom of the steaming chamber. These rollers are made to move slowly and simultaneously by worms and wheels or other equivalents, and cause the fabrics to accumulate into a pile; the latter is carried gradually to the end of the chamber whence the fabric passes from the pile out of the chamber continuously. From end to end of the chamber are fixed rails of metal or wood to prevent the piles of fabrics falling out of shape either to the right or left. The rollers are placed slightly apart to enable the steam to penetrate up to the fabric as it lies in bulk. The rollers may be covered with an endless belt of coarse cloth or blanket. The rails on each side may be formed of piping and filled with steam to prevent condensation."

The drawing shews five rollers placed in the upper part of the machine, by passing over which the cloth traverses the entire length of the apparatus five times before being deposited on the "creeper." The "creeper" shewn in the drawing consists of rollers without any blanket, but the claim reserves to the patentee the right to use an "endless belt of blanket or other suitable material."

A.D. 1876, January 24th.—No. 269.

INGHAM, OATES and HOLT, HERBERT CHARLES. "A New or Improved Method of and Apparatus for Steaming or 'Blowing' Woven Fabrics in the process of Dyeing and Finishing." This kind of "steaming" is not the same as the "steaming" of calico printers, which is only meant to fix certain colours upon the cloth, but rather forms part of the process of finishing woollen and mixed goods. As far as it can be described without a drawing it is done in the words of the specification, which are as follows:—"This invention consists in steaming or blowing woven fabrics in an inclosed vessel in which a vacuum may be formed, whereby a considerable saving of time and fuel is effected. The fabrics are wound upon hollow perforated cylinders or 'cans' in the usual manner, and one or more of these cylinders are placed

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in position on steam nozzles in the vessel, which is then closed and rendered air-tight. The air is then exhausted by an air pump or other known means, and steam admitted through the nozzles into the hollow 'cans,' which passes through the fabrics and charges the vessel with steam. The fabrics are thus thoroughly and more evenly steamed on account of the air being exhausted from the fibres of the fabric previous to the steam being introduced.

Instead of forming a vacuum by exhausting the air it may be expelled from the vessel through a valve by the steam introduced thereto."

A.D. 1876, January 26th.—No. 313.

WOLFF, JULIUS and BETLEY, RALPH. "Improvements in the Production of Aniline Dyes." This invention relates to the production of a series of dyes from aniline, with or without toluidine, and is described as follows:—"According to one mode of carrying out our invention we mix, say about 3 equivalents of aniline (with or without toluidine) with, say from about 2 to 3 equivalents of any suitable acid, by preference hydrochloric acid; into this mixture we introduce in a stream, say about one equivalent of chlorine gas, we add about one equivalent of bromine or iodine. The mixture thus obtained we heat to, say from about 220° to 230° Celsius, until a sample drawn out and dropped into boiling water communicates to the latter a brownish yellow tint. When it is ascertained that this effect is produced, the heating is continued at the temperature arrived at until a sample drawn out is found to yield up its colouring matter by repeated treatment with acidulated water at an elevated temperature. The source of heat is then removed, and from the melt thus the dye is separated by repeated extraction with water (preferably slightly acidulated with hydrochloric acid) at an elevated temperature, such extraction being repeated so long as coloring matter is dissolved. The coloring matter is precipitated from the filtered extraction liquids by means of salt or of soda, or of caustic alkalies filtered off, dried preferably with the addition of a little hydrochloric acid, and is then ready for use."

"According to another mode of carrying out our invention we mix, say about 3 equivalents of aniline (with or without toluidine) with, say from about 2 to 3 equivalents of hydrochloric or other suitable acid, and we then add, say about 1 equivalent of peroxyde of manganese or of peroxyde of lead, or of any other suitable metallic oxide capable of producing an oxydizing effect in the process. We heat and treat this mixture until the reactions hereinbefore mentioned have taken place, and extract and precipitate the coloring matter in the manner hereinbefore described."

"According to a further mode of carrying out our Invention we mix, say from about 6 to 7 equivalents of aniline (with or without toluidine) with, say from 6 to 7 equivalents of hydrochloric or other suitable acid, and we then add, say about 1 equivalent of nitric acid and subject this mixture to the treatment hereinbefore described. Or we mix, say from about 6 to 7 equivalents of aniline (with or without toluidine) with, say from about 7 to 8 equivalents of hydrochloric or other suitable acid and add to the mixture, say 1 equivalent of nitrate of soda or of any suitable nitric acid salt or oxydizing nitrous acid salt. The mixture thus obtained is subjected to the subsequent treatment for the production and precipitation of the colouring matter as hereinbefore described. Or we mix, say from about 14 to 15 equivalents of aniline (with or without toluidine) with, say from 14 to 15 equivalents of hydrochloric or other suitable acid, and add to the mixture, say about 1 equivalent of chloric acid, or bromic acid, or iodic acid or any suitable oxydizing compound of chlorine, bromine, or the like with oxygen or with 1 equivalent of the suitable salts of the acids and compounds, and these mixtures we subsequently treat in the manner hereinbefore described."

"According to another modification of our processes we mix, say from about 7 to 8 equivalents of aniline (with or without toluidine) with, say from about 6 to 10 equivalents of hydrochloric or other suitable acid, and we then add slowly, say about 2 equivalents of chromic acid in solution or a quantity of a chromic acid salt containing that amount of chromic acid

or any other suitable metallic acid salt. The mixture is subsequently treated in the manner hereinbefore described so as to obtain the colouring matters therefrom."

"According to a further modification of our processes we mix, say about 3 equivalents of aniline (with or without toluidine) with, say from 2 to 3 equivalents of hydrochloric or other suitable acid, and add to the mixture, say about 2 equivalents of copper, perchloride, or any other suitable reducible metallic perchloride. The mixture thus obtained we subsequently treat in the manner hereinbefore described. Or we mix, say from about 5 to 6 equivalents of aniline (with or without toluidine) with, say from 2 to 4 equivalents of hydrochloric or other suitable acid, and we then add to the mixture, say about 2 equivalents of sulphate of copper (or any other suitable oxydizing metallic oxysalt), and we subsequently treat the mixture thus obtained in the manner hereinbefore described. The colouring matters produced according to this Invention are soluble in water or in acidulated water and are capable of dyeing wool, cotton and other fibres in dark shades, such for example, as bluish black and grey, violet black and grey, and in all the different shades of black and grey. The less toluidine there is contained in the aniline used the bluer will be the black obtained, the more toluidine there is contained in the aniline the more violet, or brownish or yellowish are the black and grey shades obtained, the shades thus varying according to the quantity of toluidine contained in the mixture." The patentees claim as "novel and original," "the production from aniline partially or completely "neutralised by acid, and by the above described treatments, "of colouring matters soluble in water or in acidulated water."

A.D. 1876, January 29th.—No. 364.

NIXON, THOMAS. "Improvements in Pentagraph Engraving Machines." This invention is for adapting the ordinary pentagraph engraving machine used for engraving copper rollers so that it may be applied for engraving copper plates. There are two drawings, without which it would not be possible to give an intelligible description of the proposed alterations,

A.D. 1876, February 5th.—No. 468.

TOUISSAINT, CHARLES. "Improvements in Bleaching Cotton on Shuttle Cops, Bobbins or in Hanks." The process claimed includes the following operations:—

1. The introduction into each cop of a boxwood mould exactly fitting the conical aperture of the bobbin.

2. Placing the bobbins in bags, and packing them in the bleaching reservoir, where the treatment is as follows:—A vacuum is made in the reservoir for the admission of liquid chlorine, in which they remain about an hour; the vacuum is renewed, and the valve opened for the admission of water acidulated with sulphuric acid, which impregnates the bobbins. The acidulated water is decanted, and the operation is repeated two or more times. In an hour's time the reservoir is emptied, and fresh water admitted for washing, which operation lasts four or five hours, and which removes all the residues of chlorine and sulphuric acid.

3. Drying the bobbins, cops, or skeins by a hydro-extractor, or in arranging them on spindles to which a quick rotary motion is imparted.

4. Finally, drying, as usual, in a warm chamber or otherwise.

The principle of the invention consists in the process and apparatus for bleaching based on the treatment in vacuo (or vat, where the air is rarefied by a pneumatic machine) of the matters to be bleached, and by the combined action of chlorine and sulphuric acid, and in the suppression of the scalding process.

The apparatus to be employed is explained and illustrated by a drawing.

A.D. 1876, February 21st.—No. 717.

CHADWICK, JAMES. "Improvements in Dyeing and Printing Textile Fabrics." (*A Communication from James Harley, Massachusetts.*) "These improvements consist in simultaneously fixing or applying to textile fabrics, especially those made of cotton, the greens, violets, and purples known as iodine or methyl greens and aniline violets, together with the mordant or mordants destined to be dyed up in natural

or artificial colouring matters of madder, garancine, or alizarine, alone or in combination with other colouring matters, such as red woods, quercitron bark, Persian berries, or sumac, whereby styles can be produced not heretofore obtainable. The invention is carried out as follows:—I take 200 lb. of sumac, to which is added 150 gallons of water, and boil the mixture an hour or so, and then put upon a filter. After being filtered the sumac liquor is boiled down to stand at 26° Twaddell's hydrometer. For my green colour I take at the rate of 10 gallons of sumac liquor, standing at 26° Tw., 2 gallons acetic acid at 10° Tw., and 12 lb. of starch. Then the whole is boiled, and when it is cooled to about 180° F. I add at the rate of 10 oz. tartaric acid to the gallon, and when cooled down to about 120° F. I add at the rate of 2 oz. of oxalic acid to the gallon, and when quite cold I add at the rate of 3 oz. of aniline green (chemically pure) to the gallon. The colour is then ready for printing on the cloth. To make my purple I take 7 gallons sumac liquor, standing at 20° Tw., and 3 gallons acetic acid at 10° Tw., and 10 lb. of starch. Boil the whole, and when cooled to 140° F. I add at the rate of 8 oz. of tartaric acid and 4 oz. aniline purple to the gallon. This colour is now ready for printing on the cloth. I take cloth known to printers as cloth that has received a madder bleach, and pass it through a solution of chlorate of potash standing at 2° Tw., dry it, and then it is ready for printing. Pass it on to the printing machine, where the mordants intended for dyeing and the aniline green or the green and purple are printed at once, that is, at the same time. The cloth is passed through a box known as an "ageing box," and afterwards passed through silicate, arseniate, or phosphate of soda at 2° Tw., and standing at 180° F. or thereabouts. The pieces are then washed and dyed. I do not limit myself to these proportions, as they will have to be varied to suit the pattern. After having been passed through the silicate the green and purple are sufficiently fixed to pass through the dyeing and soaping operations. I have named in the above formula what is known as pure aniline purple, but the same process is applicable to any of the aniline

purples and violets, taking the corresponding strength of each. Another mode of effecting the same purpose, though not so simple as the one just described, is as follows:—In the first place I pass my cloth through the following solution previous to printing:—Gelatine standing at 2° Tw. hydrometer, silicate of soda at $1\frac{1}{2}^{\circ}$ Tw., chlorate of potash standing at 2° Tw. The cloth is then dried, and is ready for the printing machine. I may here state that the three solutions above are mixed together, and the cloth passed through them at once. To make my green colour I take four and a half ($4\frac{1}{2}$) gallons extract of sumac standing at 26° Tw., 6 lb. of starch; boil ten minutes, and when half cold I add $2\frac{1}{2}$ lb. tartaric acid, 1 lb. oxalic acid, and $1\frac{1}{2}$ lb. methyl or iodine green. This is printed on the cloth already passed through the above solution in combination with regular mordants. By this means I get an insoluble tannate of gelatine. I have named in describing my invention methyl and iodine greens, as these are the most common used of the aniline greens, but any other of the varieties of the aniline greens may be substituted, reference being had to the strength of the commercial articles substituted. After the goods are dried and aged one night I pass them through a solution of silicate of soda at 2° Tw., and heated to 180° F. or thereabout, and afterwards through arseniate of soda. The goods are then well washed and dyed to suit the pattern with different proportions of alizarine, garancine, artificial alizarine, madder, sumac, bark, berries, and such other materials as are ordinarily employed in this style of work, as is well understood by competent dyers. I am aware that indigo blues and indigo greens have been fixed in juxtaposition with ordinary madder mordants, and I do not claim this. The greens produced by my process pass through the bath just as the whites do ordinarily, and the dyeing and finishing take place just as if the portions containing the green had been white.”

A.D. 1876, February 23rd.—No. 744.

BETZOLD, GEORGE. “Improvements in the Preparation of Colours for Printing, Dyeing, or Staining; being a means of securing fastness in colours.” (*Provisional protection only.*)

This invention purports to be for the purpose of fixing mauve, magenta, and blue upon cotton and linen, and this is to be obtained by mixing with the colours "all or most of the following ingredients:—iron, vitriol, mercury, alum, gall-nuts, nitrate of silver, sulphuric acid, lime, and alcoholic or other spirit."

A.D. 1876, March 10th.—No. 1036.

GODEFROY, LÉON. "An improved process of Printing or Ornamenting Woollen or other similar Textile Fabrics. The following is the complete specification of this patent:—

The object of my invention is to give to fabrics of wool or of wool and cotton, as well as to fancy fabrics and other cloths, a new mixed appearance, which I call "Pulveribeige."

The process consists,—

1. In the application by block or cylinder printing of a dotted, granite, or other ground design to one or both sides of an unbleached woollen or woollen and cotton fabric.

2. In fixing the same by steam.

3. In submitting the fabric thus printed and fixed to fulling.

- And, 4, In finishing or dressing the said fabric.

Independently of the ground design, which can be if necessary limited to lines, stripes, or blanks, another design may be placed over it to further vary the effect of my new fabric.

Instead of printing upon the fabric the printing can be applied to the threads in skeins and to the warps, which can then be woven and fullled.

By my process of printing, fixing, and fulling I produce mixed effects directly upon the fabrics.

And having now described the nature of my said invention, and in what manner the same is to be performed, I declare that I claim the process of producing a mixed appearance or mixed effect in woollen or other similar textile fabrics by printing, fixing by steam, and fulling, substantially as herein-before described.

5. British and Foreign Patents, from the Commissioners of Patents Journal, Sept. 26th to Oct. 24th, 1876, inclusive.

Rollers for Printing.

3569. HENRY WILDE, of Manchester, in the county of Lancaster, Engineer, has given notice to proceed in respect of the invention of "Improvements in the manufacture of metal rollers for printing calico, and for other purposes."

Bleaching, Washing and Cleansing.

3896. FRANK WIRTH, of the firm of Wirth and Company, Patent Agency, of Frankfort-on-the-Maine, in the empire of Germany, for an invention of "Improvements in bleaching animal fibre."—A communication from Ferdinand Victor Kallab, Chemist, a person resident at Wiese, in the empire of Austria.—Dated 9th October, 1876.
3129. GEORGE MACKAY, of Edinburgh, in the county of Midlothian, North Britain, for an invention of "Improvements in extracting and recovering the oils, resins, and colouring matters of manufactured or waste fabrics, or from the raw materials of cotton, linen, wool, silk, or other similar substances, and in utilizing the same."—Dated 25th September, 1873.—This patent has become void.
3332. JOHN LIGHTFOOT SHORROCK, of Accrington, in the county of Lancaster, for an invention of "Improved machinery for washing or cleansing cloths and other articles, applicable also to dyeing purposes, mixing oils, and other substances or liquids."—Dated 15th October, 1873.—The £50 stamp duty has been paid upon this patent.
- 113,541. DOUINE Brothers, of Troyes, for "A machine for dyeing, washing, and bleaching textile substances."—Dated 30th June, 1876.—French patent.
- 113,990. HERLAND and GUEZENEC, for "Improvements in cleaning tissues by a chemical process."—Dated 20th May, 1876.—French patent.

**Colouring Matters, Treatment and Application,
Aniline Black.**

2390. WILLIAM WHITTHREAD, of 34, Moorfields, Liverpool,

Analyst, has given notice to proceed in respect of the invention of "Improvements in the manufacture of a pigment."

2534. ALEXANDER MELVILLE CLARK, of 53, Chancery Lane, in the county of Middlesex, Patent Agent, has given notice to proceed in respect of the invention of "An improved black dye."—A communication to him from abroad by Charles Rave, of Paris, France.
3731. JOHN BRYSON ORR, of Glasgow, in the county of Lanark, North Britain, for an invention of "Improvements in the treatment of textile fabrics, printed or dyed with aniline black, in order to prevent what is known as 'greening.'"—Dated 20th September, 1876.
3080. CHARLES DENTON ABEL, of 20, Southampton Buildings, Chancery Lane, in the county of Middlesex, for an invention of "A new blue dye or colouring matter."—A communication to him from abroad by Robert Gottheil, of Berlin, in the kingdom of Prussia, Civil Engineer and Chemist.—Dated 19th September, 1873.—This patent has become void.
3176. ALFRED VINCENT NEWTON, of the Office for Patents, 66, Chancery Lane, in the county of Middlesex, Mechanical Draughtsman, for an invention of "Improvements in the preparation of colouring matters, and in the application of the same to the dyeing, printing, and marking of textile and other fabrics."—A communication to him from abroad by Adolphe Teysonnière, of Paris, in the republic of France.—Dated 30th September, 1873.—This patent has become void.
- 40,476. E. MEUSEL, for "Obtaining colours from fossil coal."—Dated 20th September, 1876.—Belgian patent.
- 108,295. LEMOINE, for "Applying the colouring property of dichloric and fluorescent substances for ornamentation."—Dated 29th May, 1876.—Certificate of addition to French patent.
- 113,695. WILLM, BOUCHARDT, and GIRARD, of Paris, for "Colouring substances."—Dated 7th July, 1876.—French patent.
- 113,718. PETIT, of Villefranch, for "Violet aniline for fast dyes on cotton."—Dated 17th July, 1876.—French patent.

Printing and Dyeing Processes.

1654. WILLIAM MORGAN-BROWN, of the firm of Brandon and Morgan-Brown, Engineers and Patent Agents, of 38, Southampton Buildings, London, and 13, Rue Gaillon, Paris, for an invention of "Improvements in the manufacture of ornamental textile

fabrics."—A communication to him from abroad by Samuel Barlow, of Lawrence, Massachusetts, United States of America, Colour Master.—Dated 20th April, 1876.—Sealed.

2048. JOE FROST, of Huddersfield, in the county of York, Chemist, and JOHN WALMSLEY, of Mirfield, in the same county, Printer, have given notice to proceed in respect of the invention of "Improved means or methods of obtaining two or more colours on piled fabrics, or on material intended for such fabrics, with a view to imitate the skins of animals or produce designs thereon, such means being also applicable to produce different effects on natural skins or furs."
3732. JAMES SHAW, of Galashiels, in the county of Selkirk, North Britain, Manufacturer, for an invention of "Improvements in rollers for expressing liquid from textile materials, yarns, and fabrics."—Dated 25th September, 1876.—Provisional protection has been granted.
3121. WILLIAM WHISTON, of Langley, near Macclesfield, in the county of Chester, for an invention of "Improvements in dyeing and printing silk and other woven fabrics."—Dated 24th September, 1873.—This patent has become void.
6. J. CARREY, of Mulhouse, for "A process for giving the designs of prints the appearance of woven designs."—3 years.—Dated 6th May, 1876.—Prussian patent.

The following are French Patents:—

- 105,949. DAVID Brothers, for "A reel for dyeing and scouring machines."—Dated 7th December, 1875.—Certificate of addition.
- 112,933. SCHLUMBERGER, jun., and Co., for "A machine for printing fabrics, paper, &c., with any number of colours."—Dated 17th May, 1876.
- 112,966. ROUSSEL, of Roubaix, for "Dyeing and finishing tissues."—Dated 1st June, 1876.
- 113,423.—RADDE, for "Improvements in printing in colours upon paper or other fabric or material."—Dated 22nd June, 1876.—(English patent, 30th May, 1876.)
- 113,486. IMBS, for "Manufacturing prints in imitation of terry or cut velvet."—Dated 24th June, 1876.
- 113,607. DELHARPE, for "A machine and process for print-dyeing."—Dated 6th July, 1876.
- 110,688. RICHARD, of Paris, for "A machine for printing so-called 'framed stuffs.'"—Dated 8th July, 1875.

Treatments of Yarns, Hanks, Skeins, etc.

3603. EUSTACE WIGZELL, and JOSEPH POLLET, of the firm of Timothy Bates and Company, of Sowerby Bridge, in the county of York, Engineers, for the invention of "Improvements in machinery or apparatus for drying skeins or hanks of wool or other fibrous material."—Provisional protection has been granted.
3929. WILLIAM CRAWFORD, of Paisley, in the county of Renfrew, North Britain, Dyer, for an invention of "Improvements in bleaching, washing, and dyeing yarns in hanks, and in the machinery or apparatus employed therefor."—Dated 11th October, 1876.—Provisional protection has been granted.

Treatments of Wool and Silk.

2505. EDWARD GRIFFITH BREWER, of Chancery Lane, London, has given notice to proceed in respect of the invention of improvements in bleaching and purifying wool."—A communication to him from abroad, by Messrs. Daudier, Père et fils, of Paris, France.
2947. CHRISTOPHER WEBB SMITH, of Barnwood, near the city of Gloucester, Chemist, has given notice to proceed in respect of the invention of "Improvements in and apparatus for scouring or cleansing woollen cloth, yarns, and wastes, and in recovering valuable products from the materials which have been used in conducting the said scouring or cleansing."

The following are Belgian Patents.

- 40,308. J. RAULIN, a patent of improvement for "Improvements in the treatment of wool, chiefly applicable for cleaning by means of sulphuric acid."—Dated 24th August, 1876.—(Original patent, 1st March, 1876.)
- 40,309. J. RAULIN, a patent of improvement for "Improvements in the treatment of wool, chiefly applicable for cleaning by means of sulphuric acid."—Dated 24th August, 1876.—(Original patent, 1st March, 1876.)
40320. J. DABERT, for an imported invention of "A machine for printing or dyeing wool, &c. by sections."—Dated 25th August, 1876.—(French patent 23rd August, 1876.)
- 40,400. G. RYDILL, for an imported invention of "Improvements in preparing wool, cotton, silk, &c., for cleaning and extracting the vegetable fibres therefrom."—Dated 7th September, 1876.—(English patent, 4th March, 1876.)

- 40,401. G. RYDILL, for an imported invention of "Improvements in utilizing waste heat in drying wool, hair, &c., chemically treated for removing vegetable or strange substances therefrom."—Dated 7th September, 1876.—(English patent, 4th March, 1876.)

The following are French Patents.

- 100,379. MRS. JOLY, for "Improvements in incinerating filth in wool, &c."—Dated 16th May, 1876.—Certificate of addition.
- 102,223. DELAMARE, Son, and Co., for "Improvements in cleaning cloth, woollen, by a chemical process."—Dated 20th December, 1875.—Certificate of addition.
- 110,736.—DETRE, of Sedan, for "Dyeing curled wool in slubs on beams or frames that can be reduced."—Dated 23rd December, 1875.
- 109,921. MICHEL, for "Carbonizing vegetable matter in wool."—Dated 12th July, 1876.—Certificate of addition.
- 110,574. GRISON, of Lisieux, for "Dyeing, mordanting, and cleaning woollen stuffs by one operation."—Dated 14th December, 1875.
- 110,714. QUIROGA-BARCIA, for "A process for scouring or ungumming raw textile fibres for lessening their volume and facilitating freights."—Dated 16th December, 1875.
- 110,727. BERTHET, for "A machine for beating and washing silk."—Dated 30th December, 1875.
- 110,738. DUCHEZ, of Comme d'Yzieux, for "A machine for shaking dry and tentered silks after dyeing."—Dated 27th December, 1875.
- 111,802. LALOUEL DE SOURDEVAL, for "Scouring waste fat wool."—Dated 11th May, 1876.—Certificate.
- 113,159. NICHOLS, for "Improvements in machines or apparatus employed for washing or wringing wool and other fibres."—Dated 2nd June, 1876.
- 113,177. DAUDIER, sen. and jun., for "An antiligneous bath for bleaching and purifying wool."—Dated 3rd June, 1876.

Finishing Processes.

2956. JOSEPH KEIM, of Tharm Alsace, Allemagne, has given notice to proceed in respect of the invention of "Improvements in machinery for stretching and drying textile fabrics."
3947. PAUL MAGNER, of Percy Street, in the county of Middlesex, Analytical Chemist, for an invention of "An improved process

of treating vegetable fibres to impart to them a silky appearance."

—Dated 12th October, 1876.

2787. WILLIAM HARPER, of the firm of Messrs. Eden and Thwaites, of Bolton, in the county of Lancaster, Bleachers and Finishers, for an invention of "Improvements in machinery or apparatus for suspending fabrics in drying stoves."—Dated 25th September, 1869.—This patent has become void.

2792. JAMES WORRALL, of Manchester, in the county of Lancaster, Dyer, and JOHN KERSHAW, of Wadsworth, in the parish of Halifax and county of York, Spinner, for an invention of "Improved machinery for folding piece goods."—Dated 25th September, 1869.—The stamp duty of £100 has been paid upon this patent.

3445. JOHN ROBERTSON, of Nitshill, in the county of Renfrew, North Britain, Engineer, for an invention of "Improvements in compressing air for burning in combination or mixture with gas or inflammable vapour in apparatus for finishing textile or other fabrics or in other apparatus where heat is required, and in the means employed therefor."—Dated 23rd October, 1873. The stamp duty of £50 has been paid upon this patent.

113,015. Miss D'HERDT, for "A cylinder for plaiting stuffs."—Dated 22nd May, 1876.

96,284. PIERRON and DEHAITRE, for "A machine for dressing woollen, silk, and other tissues."—Dated 24th May, 1876.—Certificate of addition to French patent.

99,530. PIERRON and DEHAITRE, for "Widening fabrics."—Dated 29th May, 1876.—Certificate of addition to French patent.

113,619. HEILMANN-DUCOMMUN and STEINLEN, of Belfort, for "A new arrangement of chains in tenters or apparatus for drying tissues."—Dated 11th July, 1876.

108,820. DELAMARE and LEMAIRE, for "Finishing cloth and fancy articles."—Dated 14th July, 1876.—Certificate of addition to French patent.

Erratum in the October No. of the Textile Colourist.—The Editor has to thank Mr. R. Pickup, of Bowker Bank, for pointing out an error which occurs in the second note on p. 173; line 5 from bottom instead of 770,000 read 77,000; and in line 4 from bottom, instead of *nine-tenths* read *nine-hundredths*.

THE TEXTILE COLOURIST.

No. 12.]

DECEMBER, 1876.

[Vol. II.]

1. Materials for a History of Textile Colouring, No. 4.

SOME time prior to the year 1756, the Honourable Board of Trustees for the improvement of fisheries and manufactures in North Britain engaged or desired Dr. Francis Home, Fellow of the Royal College of Physicians in Edinburgh, to compose a Treatise upon Linen Bleaching. It was read in the shape of lectures to the bleachers of Scotland, and illustrated by experiments as far as possible; and afterwards, at the request of the bleachers, was published. The work is entitled "Experiments on Bleaching, by Francis Home, M.D." It is dated Edinburgh, 1756. On p. 19, the author says it is "an attempt to reduce to a regular system, an art, in which nothing has yet appeared in any language, in which we have even no account of the common practice." We have seen somewhere a reference to a book of still earlier date in the Dutch language upon linen bleaching, but have never met with the work, nor is it found in the lists of books upon the subject in our principal libraries. This work may therefore be looked upon as the earliest available work upon the subject. It was written by a learned and accomplished man, who had taken much trouble to investigate it, and, as it appears, had received considerable facilities for pursuing it at the hands of the manufacturers practically engaged in bleaching. It is a most valuable record of the state of the

art in the middle of the last century, and well deserves a detailed notice.

Dr. Home treats the whole subject from a broad point of view, and in the commencement refers to the influence which government has upon the progress of manufactures. His views, it will be seen, are those which still hold good in the majority of countries where it is felt desirable to establish new industries, and though they have been of late years discarded as impolitic in this country, were, at the time of the writer, held as indisputably sound, and to a greater or less degree practically acted upon. He says:—

“The influence of the government consists in encouraging home manufactures, by granting protection, privileges, immunities, and bounties to such as carry them on; by taking off all duties on the materials used in them; by establishing proper trustees to have the inspection of them, and companies with suitable privileges; by settling proper funds to be distributed in rewards to those who excel; by not making it too burthensome and expensive for the manufacturers to obtain good laws; and by a proper regulation of the fashions at their source.

“But all these advantages are of small avail, if a ready market is not opened; for it is an axiom in trade, that manufactures increase only in proportion to the demand for them. Here then will the wise politician be again discovered, in discouraging all foreign manufactures of the same kind, by prohibitions, or high duties equivalent to them.”

He proceeds to thank the existing government for acting upon these principles, which had caused more to be done in the few years just past than in all the ages before, so that even in the confusion which attended the political confusion of 1745, the linen trade had gone on extending. The leading merchants must also, he tells us, co-operate, and he praises in the highest terms the well judged regulations of the Irish linen manufacturers and merchants in establishing the Linen Hall in Dublin, which afforded a “constant market for foreign merchants, and a constant check to the frauds of private dealers.” He praises also the action of the Board of Fisheries

and Manufactures in Scotland, which was constituted in 1727, for the way in which they had acted in directing the spirit of industry in that country.

The Irish linen bleachers are warned that from want of care in the bleachfield, or from ignorance or fraud that their trade "will, nay perhaps has already, come into some disrepute; and must at last suffer if the Irish do not alter their method of bleaching." In Scotland it is said they generally followed a better method, not from a greater knowledge of the art, or that they can claim any merit for it, but that it was owing to their vicinity to Holland. Dr. Home then shews how much chemistry could do to assist linen bleachers. We know how much this science did do within the lifetime of men who may have heard Dr. Home's lectures, and recalling to mind the services of the author himself, of Scheele, Berthollet, and Le Blanc, it is not without interest we read what he says upon the connection of chemistry with dyeing.

"Let us take a review of the dependence which these arts have on chymistry. Dyeing cannot be carried on without it. The instruments with which that art works are quick-lime, alkaline and acid salts, solutions of tin and iron in acids, and neutral salts, as alum, salammoniac, and tartarus vitriolatus. Without the assistance of these salts very few colours can be struck on either woollen, linnen, or cotton; but with their assistance, all the colouring particles are separated from the water in which they are dissolved, and fixed on the surface of these bodies. The durableness of colours, and their resistance against the effects of sun and moisture, are to be explained only from the properties of these salts. In the solutions and mixtures of chymistry, many beautiful colours, which were never heard of in the art of dyeing, arise, are changed, or destroyed. . . . I know of no trade which is so entirely the object of chymistry as bleaching, and none that has been so little considered in that light. For what are steeping, bucking, souring, washing with soap, alternate wetting and drying, but so many processes that are carried on by these powerful chemical agents, heat, and dissolvents? What is the end proposed but the dissolving and carrying off, by means of acid and alkaline salts, most powerful menstruums, somewhat which gives

the cloth its present colour? and what way more certain to carry off whatever is loosened, than the evaporation of water by heat, which is a species of distillation performed in the open air?"

The last paragraph intimates the theory which pervades generally the whole treatise; that is, that the colouring matter of raw linen is made volatile and exhales away in the air, by reason of the action of the various chemicals upon it. It must be remembered that Dr. Home wrote more than one hundred and twenty years ago, when the state of chemical knowledge was very different from what it is now, and at a time when several false theories had a firm hold upon the scientific men, oxygen had not been discovered, nor carbonic acid, nor the alkaline metals; and the acutest minds, in trying to explain the phenomena of chemistry, were groping in the dark. At this time it seems pretty well proved that the action of the chemical agents in bleaching is to change the insoluble colouring matters of raw linen into substances which can be washed away with water, and that the action of air, or evaporation when applied, is to help in such a result.

The actual constitution of the alkaline ashes was in Dr. Home's day entirely hidden, and he frequently refers to the want of knowledge upon this matter, and directed a great portion of his experiments to ascertaining what they really were. He says, "If this point was once ascertained, the theory of bleaching would rest on a more certain foundation than at present. For what certain theory can be established with regard to the operation of those ashes, when we know not what those ashes are?"

"What if these bodies are not simple alkaline salts? For aught we know they may not, but may be a composition of different substances. And what if we discover by chymical experiments their composition? If this happens to be the case, we may perhaps be able to make these ashes at a much cheaper rate in our own country than what they cost us when imported from abroad. The enquiry is worthy of the utmost attention; and, if successful, cannot fail to be of great importance to this country. It costs, as I am told, Great Britain and Ireland £300,000 for ashes every year. It is difficult to

say to what a sum that commodity may amount; nay, it is impossible to assure ourselves that we will procure it at any price, when we are told that the ashes were monopolised by two Dutch merchants three years ago, and retailed again to us at a double or triple price. Our manufacturers could not have subsisted during the late war with Spain, unless an order of the King and council had passed, allowing the importation of Spanish pot ashes."

For many a long year after this was written the British bleachers depended upon foreign ashes, which were uncertain in their supply, and irregular in their price and quality. But the enquiry into the nature of these ashes so urgently pressed by Dr. Home, and at length and at considerable intervals of time successfully accomplished by the labours of Black, Davy, and Le Blanc, has achieved what he hoped for, and, not only (to quote his own words) do we "make these ashes at a much cheaper rate in our own country than what they cost us when imported from abroad," but we may be said to be able to supply the whole world with these very ashes, cheaper and better than they can be obtained from their old sources. In another part the author quotes as a leading maxim a passage from Hippocrates, which seems to include the whole aim and intent of experimental enquiry in the industrial arts; "that the design and labour of science ought to centre in discovering what is yet unknown, and may become when known, useful to society; and likewise in completing what was left by others imperfect." Upon this maxim Dr. Home worked, and by a method, and with results clearly and frankly enough set forth.

"There is no way to promote the art of bleaching, which is entirely carried on by the operation of different bodies, but that of experiment, and that alone I have followed. Every other method of advancing the arts is now justly derided. It is indeed laborious to the undertaker, and cannot be accomplished without accuracy and length of time; it is often unpleasant to the reader. But, as the former has not deterred me from making the experiments, the latter shall not hinder me from narrating them as they were made. No doubt can remain when the experiment is before

our eyes. I expect this of others, and therefore I shall follow it myself.

Dr. Home describes in detail the process of bleaching linen as carried on at the date of his experiments. There were two general methods, the Dutch and the Irish. The Dutch method was followed for fine cloth and used by the most skilful bleachers; the Irish method was cheaper and used for coarse cloth. We give an abstract of the two processes as the account in the original is too long to be inserted in full.

In the Dutch process for fine linen, the first process is to fold up the linen, each piece distinct, and lay the pieces in a large wooden vessel, into which is thrown blood-warm water, or a mixture of equal parts water and ley which has been used for white cloth only, or water with rye meal or bran mixed with it; when the whole is thoroughly wet, the vessel is closely covered up, fermentation sets in, and when the air bubbles cease, and the scum first formed begins to subside, which may be in thirty-six or forty-eight hours, the cloth is taken out; it is then washed and spread upon the field until quite dry. The bucking next follows; the first ley is made from 170 Scots gallons of water made to boil, and then there is added 30 lb. blue and as much white pearl ashes, 200 lb. of Marcroft ashes (or instead of these, 300 lb. of cashub), 300 lb. of Muscovy or blanc ashes. This forms the mother ley; the bucking ley is made by taking 2 gallons of the mother ley to 38 gallons of water and 2 lb. soft soap, or the soap is replaced by some of the white linen ley. The linen is treated by the ley by packing it in a wooden vessel with a tap at the bottom, and pouring on the ley blood-warm, drawing it off at the bottom into a heating copper, and after warming pouring it on the linen again; this is repeated for six or seven hours, the heat of the ley being gradually increased until at the end it is thrown boiling hot on to the cloth.

The cloth is next, and apparently without washing, spread on the grass and for six hours kept watered so that it does not go dry; afterwards watered when dry spots begin to

appear ; not watered in the night-time unless it be a very drying night ; next day watered if the weather is very dry ; taken up dry if the green is clean, if not it is rinsed and is ready for another bucking. This operation of bucking and watering is repeated from ten to sixteen times, increasing the strength of the ley up to the middle bucking, and from that gradually decreasing.

It may be observed that this system was most tedious and ineffective simply from mechanical causes, but no better was known. If the process was attempted to be pushed by using hotter liquids or stronger leys, bad results were frequent. This method of simply pouring the ley upon the cloth would distribute it very unequally, and it could be only after ten or more changes of position that it could be hoped that every part of the cloth had received its share of the hot ley.

The bucking was followed by the souring. The cloth was considered fit for souring when it was "mostly freed from the sprat or outer bark of the lint;" the cloth was covered with buttermilk and pressed down by two or three men barefooted. Sours made with bran or rye meal and water are often used. A large quantity of cloth being thus impregnated with the sour liquid was then covered up, fermentation took place; when air bubbles ceased to appear the operation was finished. The souring took *five or six days*, after which the cloths were washed and went on to the next process.

This was a washing by hand with soap and water, or rather a rubbing of soap and water into the selvedges of the cloth.

The bucking is now repeated with stronger leys than at first. There is nothing more to be said of the Dutch process but that the bucking, grassing, washing, souring, and soaping were continued and repeated until the cloth was white.

In the Irish process the cloth was steeped as in the Dutch process. The bucking was done by actually boiling the cloth in a somewhat weaker ley, the boiling being continued for two hours ; then the cloth spread on the field and watered. The boilings and grassings were continued and repeated six

or seven times, or until from the appearance of the cloth it seemed ready for souring.

“The common method of souring coarse linen is to mix some warm water and bran in the vat ; then put a layer of cloth ; then more bran, water, and cloth and so on till the cave is full. The whole is tramped with men’s feet and fixed as in the former process. One thousand yards of cloth, yard broad, require between 4 and 6 pecks of bran. The cloth generally lies about three nights and two days in the sour. Others prepare their sour twenty-four hours before by mixing the bran with warm water in a separate vessel, and before pouring it on the cloth they dilute it with a sufficient quantity of water.”

About three boilings in ley after souring was held sufficient for coarse cloth, which was then “starched, blued, dried, and bittled in a machine made for that purpose, which supplies the place of a calender, and is preferred by many to it.”

It is remarked that the Scotch process for treating coarse cloths was very nearly the same as that used in Ireland for both fine and coarse cloths ; in Ireland the bleachers, however, used only kelp or cashub as alkaline materials, preferring the cashub.

This sketch shews the precise state of linen bleaching when Dr. Home engaged in his experiments upon it. He next proceeds to throw what light he can upon the reason of the different operations, and we shall follow him in that course.

The “green” linen is very foul, chiefly from the dressing composed of tallow and “sowen,” which is a kind of flummery made of bran, flour, or oat meal seeds. The steeping is designed to remove this ; cold water would act too slowly, very hot water might coagulate and fix the substance. The effect of fermentation is described in a way which shews how it was viewed by the writer. The acetic acid is not supposed to be formed, but set free from a combination, as may be gathered from the following passage :—

“The acid salts are no sooner separated by the acetous fermentation from the absorbent earth, which made them not perceptible to the tongue in their former state, than they are united to the oily par-

ticles of the tallow, which likewise adhere superficially, dissolve them, and render them in some degree miscible with water. In this state they are soon washed off by the intertine motion of the liquor."

[*To be continued.*]

2. *New Method for ascertaining the exact quantity of Pure Anthracene contained in Crude Anthracene.**

BY MEISTER, LUCIUS, AND BRÜNING.

THE experience gained during the last few years with regard to anthracene testing has induced us to abolish our old test of October, 1873, and the appendix of 1874, and to issue a new and improved method as follows: Take 1 grm. of anthracene, place it in a flask of 500 c.c. capacity, add to 45 c.c. of glacial acetic acid and heat to ebullition. To this solution, which is kept boiling, add drop by drop a solution of 15 grms. of chromic acid in 10 c.c. of glacial acetic and 10 c.c. of water.

The addition of the chromic solution should occupy two hours, after which the liquid is to be kept boiling for two hours longer, four hours being required to complete the oxidation.

The flask, with its contents, is to be kept standing for twelve hours, then mixed with 400 c.c. cold water,† and again kept standing for three hours.

The precipitated anthraquinone is now collected on a filter, and washed first with pure water, then with boiling dilute alkaline solution, and finally with pure hot water. The quinone is now washed from the filter into a dish and dried at 100° C. It is then mixed in the same dish with ten times

* Chemical News, October 20th, 1876.

† The increased quantity of water added insures the complete precipitation of the anthraquinone and the correction formerly made is no longer necessary.

its weight of fuming sulphuric acid of 68° B. (sp. gr. 1.88 or 176° Tw.), and heated to 100° C. for ten minutes on a water bath. The quinone solution thus obtained is poured into a flat dish, and kept for twelve hours in a damp place to absorb water.

Then add 200 c.c. of cold water to the contents of the dish, collect the precipitated quinone on a filter, and wash first with pure water then with boiling alkaline solution, and finally with pure hot water.

The anthraquinone is now placed in a dish, dried at 100° C. and weighed. After volatilizing the quinone by heating the dish, it is weighed with the particles of coal and the ash.

The difference between the two weights gives the weight of anthraquinone obtained, as it is to be calculated in the usual manner into anthracene.

In the number of the Chemical News following the one from which the above article is taken, Dr. F. Versmann writes upon the same subject. He had previously, in a paper read before the Society of Arts, March, 1874, expressed his opinion that the previous quantitative test for anthracene given by the same firm of Meister, Lucius, and Brüning was untrustworthy. It involved an allowance, perfectly arbitrary, of 1 per cent. for solubility of quinone, which, according to Dr. Versman, made the whole process illusory. "The new test," says Dr. Versmann, "differs from the previous one merely by an increase of the oxidizing agent—chromic acid and its solvent acetic acid and water—and by the treatment of the quinone with fuming sulphuric acid instead of with potassium permanganate, and subsequent volatilization of the remaining quinone."

The publication of the new method has induced Dr. Versmann to give some results of unfinished researches upon this matter, he says, "after boiling a sample of anthracene with chromic acid solution and allowing the mixture to stand for hours, long, well defined crystals separate, and on adding water a further separation takes place, not in the form of crystals, but of an amorphous powder. The product collected

on the filter is always a mixture of crystals and powder, part of the last of which is again removed by potassium permanganate and potassium hydrate.

"This observation induced me to collect the crystals and powder separately, and ascertain their nature by practical tests applicable for commercial analyses. As such, I adopted above all, the melting- and solidifying-points, and then the action of potassium permanganate and potassium hydrate."

"The determination of the melting- and solidifying-points I look upon as most important and valuable, and I can only express my surprise that it has not been introduced long ago, especially as it formed so important a part in the alcohol and bisulphide test."

Dr. Versmann then refers to a long table, in which the results of testing thirty various samples of anthracene are given. First is given the quantity of so-called quinon obtained by the oxidizing agent without correction, it represents the mixture of crystals and powder precipitated by water, and runs from 11.4 for a low quality up to 68.5 for a high quality. In another column is given the weight of crystals distinct from the powder, the weight of which occupies another column. The relative weights of powder and crystals vary very much. In the first case there is 6.6 crystals to 4.8 powder, and in the last case 63.2 crystals to 5.1 powder. The melting- and solidifying-points of the whole quinon, the crystals, and the powder are also separately given. The melting points of the mixture range from 268° to 283° . The melting points of the crystals separately does not shew so much variation, many samples melting at 277° and 278° , the extreme range being from 274° to 279° . The melting point of the powder has a much greater range. In eleven samples the powder did not melt at 300° , and in others melted at 245° . Another column shews the relative quantity of potassium permanganate which was required to be added to each of the three bodies—mixture, crystals, and powder, so as to leave a distinct colouration after boiling with them. The crystals require from two to six drops of a 5 per cent. solution; the mixtures required from six to twenty-five drops; and the

powder from five to twenty-eight drops. Dr. Versmann proceeds:—

“As to the operation itself, the first result was obtained by the usual test with appendix. In the separation of crystals and powder the solution was allowed to stand over night; the crystals were then collected on a small filter, and the solution allowed to run off to the last drop, before the crystals were washed with water, until the filter and filtrate were perfectly colourless. The filtrate was then diluted to 600 c.c., and after two hours' standing the powdery precipitate was also collected on a filter; both crystals and powder were then treated with potassium permanganate and potassium hydrate.

I have long adopted an increased addition of water, but for a different reason than the one now stated by Messrs. Meister, Lucius, and Brüning. I have always doubted the accuracy of adding 1 per cent. of quinon, supposed to be retained in solution, and I have satisfied myself on that point by actual experiment. I have frequently evaporated the green solution to perfect dryness, and exhausted the dry powder with benzol and alcohol, but I have never succeeded in separating real quinon. The larger quantity of water merely separates the powder more completely, which no doubt accounts for the increased quantity of potassium permanganate used with the powder.

The conclusions drawn from this table, I may state as follows, viz.:—

(1) The total of crystals and powder in all cases very nearly agrees with that of the mixture; no loss is incurred by the separation.

(2) The melting- and solidifying-point of the mixture, *i.e.*, of the usual test, is mostly suspicious, in many cases a direct indication of undoubted impurity of the quinon.

(3) The melting- and solidifying-points of the crystals alone are much more uniform; the product is pure quinon.

(4) The powder in almost all cases is no quinon at all; in eleven cases out of thirty it does not melt at 300° C., but blackens and remains solid; in eleven other cases the mean of the two points is below 270° C., and in several of the other

cases the melting- and solidifying-points were only partial or indistinct at the points indicated.

(5) The effect of potassium permanganate is uniformly very trifling upon the crystals, very considerable upon the powder, and exactly the same is the case with potassium hydrate; while the mixture often imparts distinct colouration to the solution and becomes itself lighter in colour—from orange to pale straw-yellow—the crystals alone scarcely shew any change, but the powder invariably gives a strong colour to the solution.

(6) While the crystals may safely be taken as pure quinon, the question arises whether the powder always consists of nothing but impurities, or whether it still retains some quinon, as in a few cases the melting-point tends to indicate.

Although I have not completed my experiments in that direction, I shall shortly be able to definitely settle this point by practical tests.

But I think it advisable not to delay the publication of my results hitherto obtained, as I am satisfied of the correctness of separating crystals and powder and of its undoubted advantage over the other known test.

I have meanwhile brought my test into practical working by taking the crystals as pure quinon, and by considering the powder as valueless impurity in all cases where the melting- and solidifying-point is below 270° or above 280° , and by adding the powder to the crystals as quinon whenever these two points range between 270° and 280° .

This compromise, for such I admit it to be at the best, has given general satisfaction to those who had it tried; and although I hope in a short time to complete my investigation, I meanwhile propose the above test, which, briefly stated, is as follows:—

Boil 1 grm. of the sample for four hours with 15 grms. of chromic acid dissolved in 10 c.c. of water; allow it to stand for twelve hours, collect the crystals on a small filter, and let the solution run off to the last drop; then wash the crystals with boiling water till the filter and filtrate are quite colourless, dilute the filtrate with water to 600 c.c., let stand for two

hours, and collect the powdery precipitate on a filter and wash well. Then treat both crystals and powder—separately of course—with potassium permanganate and potassium hydrate as hitherto, collect each on a double filter, dry and weigh, but do *not* add the correction; then take the melting- and solidifying-point of both. The crystals to be taken as pure quinon, the powder also to be taken as quinon if melting- and solidifying-points range between 270° and 280° , but as valueless impurities if these two points are below 270° or above 280° .

This test is more reliable, and more just to buyer and seller, than either the usual quinon test or the one now proposed by Messrs. Meister, Lucius, and Brüning."

In a continuation of his communication, Dr. Versmann insists that, though his test may cause some confusion as indicating a lower percentage than the ordinary test, it is more correct and trustworthy. He remarks that the tests for the value of anthracene have been progressive in reducing the percentage, at the same time the price per cent. has increased. He considers that the better qualities are really the cheapest, and enters into some details of experiments upon pressing and washing low qualities of anthracene, in which it is shewn that the percentage yield of crystals can be greatly increased, and that of powder decreased by proper treatment; but it would appear that there is a great loss of the whole weight of crude anthracene in these treatments.

3. Upon the "Greening" of Aniline Black.*

M. R. GLANZMANN made some experiments with reference to this subject of greening, which, though not leading to any distinctly practical result, attack the question from an entirely different side, and are worth including in this collection of

* Continued from p. 276.

researches. He remarks that the only remedy against greening which had been recommended was to print a very strong black. But the difficulty which meets the colourist in attempting this is, that concentrated blacks are liable to weaken and even to tender the cloth printed upon.

Then it naturally occurred that it might be possible to prepare the black before printing, to develop it away from the cloth, and apply it ready formed in the state of a black lake or precipitate. Different methods can be pursued for preparing precipitates of aniline black, these precipitates or lakes having different characters, according to their mode of preparation.

M. Glanzmann prepared five different kinds of precipitated black. They presented differences as far as regards composition and appearance, but were alike in being fast and stable colours. All of them completely resisted the action of acids, alkalies, and light. They shewed no inclination to become green, even when reduced by dilution to the condition of light greys. The grey shades yielded by these black lakes are as fast as the carbon greys from lamp black, without having their unpleasant yellowish shade. They can be used in many cases without any blue admixture.

The first black was obtained as follows :—

- 1 gallon of water.
- 1 lb. muriate of aniline.

Heat to the boiling point, and add, little by little,

- 5 oz. sulphate of copper, in
- 6 lb. of water.

Continue to heat, and add slowly a solution of

- $\frac{1}{2}$ lb. bichromate of potash, in
- 6 lb. water.

Keep at the boiling point for three hours ; add an abundance of water, and wash by decantation ; throw upon a filter and wash further with water containing ammonia.

- Drain the precipitate down to ... $4\frac{1}{4}$ lb.
- The paste then contains about... $3\frac{1}{4}$ lb. water
- and 1 lb. dry black.

The dry black is composed of ... 20 per cent. of organic matter
and 80 per cent. of oxide of copper
and chromium.

This proportion of oxides is very large, and cannot be otherwise than injurious to the colour. In order to avoid this inconvenience he made another preparation without copper salt, which gave an improved result.

No. 2 Black.

1 gallon of water.

1 lb. aniline oil.

13 oz. bichromate of potash.

Dissolve by heating up to 140° F., and add, little by little,

1 lb. muriatic acid, at 34° Tw., mixed with

4 lb. water.

Heat to boiling for two hours, until the mass which thickened at first separates or breaks. Wash by decantation, put upon a filter, and drain down to 5 lb.

This paste contains 3¼ lb. water
and 1¾ lb. dry black.

The dry black is composed of ... 60 per cent. organic matter
and 40 per cent. oxides of chromium.

Here again the proportion of oxide is exceedingly high, and moreover the precipitates are not nearly so fine as they should be. On the large scale it would be necessary to use much more dilute solutions.

It is not necessary to use salt of aniline in order to obtain the black; a simple oxidation of the organic base itself yields it. Aniline oil is soluble in tolerably large quantities in solution of bichromate of potash, and by keeping such a mixture for several hours at the boiling point the black is obtained. The quantity of black precipitate obtained by this process varies according to the quantity of aniline employed, and especially according to the proportion of bichromate.

Weak solutions of aniline do not give any black; by leaving such solutions at rest for several days, it is remarkable to see a large quantity of brown oxide of chromium deposited,

which by ignition becomes green. The same precipitate takes place in the filtrate from the precipitates when the liquor has not been heated sufficiently long.

The black lakes obtained by this method are as permanent as those obtained from the salts of aniline. They still contain a large quantity of oxide of chromium, and are not sufficiently dense to be readily available in printing.

The oxide of chromium is not found simply as a mechanical mixture in these black lakes, it would seem to be combined with the organic matter, which would explain their great stability. In the analysis of the lakes the quantity of oxide of chromium found is nearly constant; in order to extract it completely the black must be destroyed; thus, by treating it with aqua-regia, there is left nothing but a puffy mass of a brown colour, which burns away without leaving any residue.

M. Glanzmann made three different blacks by direct oxidation of aniline, the proportions employed were as follows :—

No. 3 Black.

- 1 lb. aniline oil.
- 1 lb. bichromate of potash.
- 1 gallon water.

Heat and boil for three hours, wash by decantation, and drain upon the filter to 1 lb.

The paste contains 74 per cent. of water and
26 per cent. of dry black.

The dry black is composed of 58 per cent. organic matter
and 42 per cent. oxide.

No. 4 Black.

- 1 lb. aniline oil.
- 2 lb. bichromate of potash.
- 1 gallon water.

Treat as before, and drain by filtration to 2 lb. of lake.

The paste contains $76\frac{1}{2}$ per cent. water
and $23\frac{1}{2}$ dry black.

The dry black is composed of 57 per cent. organic matter
and 43 per cent. oxides of chromium.

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No. 5 Black.

- 1 lb. aniline oil.
- 4 lb. bichromate of potash.
- 2 gallons water.

Proceed as before, and drain down to 3 lb. of lake.

This paste contains 72 per cent. water
and 28 per cent. dry black.

The dry black is composed of 53 per cent. organic matter
and 47 per cent. oxides.

By comparing the quantities of black obtained by the three different processes, it will be found that the weight increases directly as the proportion of bichromate of potash. The composition of the lakes is not greatly different, and the amount of oxide of chromium present in them nearly the same in every case.

These results have, however, no bearing at present upon the question of the greening of printed aniline blacks; precipitates which would have to be fixed by means of albumen would make this style of print much too expensive, besides presenting special difficulties in the working.

But, by studying the formation of aniline black from another point of view, we shall most probably be able to modify its production upon the tissue itself. One fact is proved by the experiments here related, which is, that aniline is capable of giving a black perfectly fast, and resistant to the action of light, alkalies, and acids. This gives hopes of further progress, and is an encouragement to proceed with our experiments.

4. *Cantor Lectures on Wool Dyeing.**

IN the fourth lecture of his course Mr. Jarmain commences with Logwood, which, he says, is the most important of all

* Continued from p. 261.

dyestuffs after madder, and for wool dyeing much more important than even madder. In former times logwood colours had an ill repute; they were said not only to be loose and bad colours, but to corrode and rot the cloth dyed with them. But now, as Mr. Jarman says, "the use of proper mordants and a better knowledge of the properties of the colouring matters, have enabled dyers to obtain such fast and permanent colours with it, that the ban under which it formerly lay, arising from the fugitive nature of the colours obtained by the dyers who first used it, has long since passed away."

We pass over and omit the general and scientific remarks of the lecturer upon this dyewood, to give what he says upon its practical treatment and application in dyeing.

"It is prepared for the use of the dyer in the three following forms:—1st, in chips; 2nd, ground or in raspings; 3rd, as an extract, which is the solid or semifluid residue obtained by evaporating the decoction of the wood.

The colouring matter is developed by moistening the chips and raspings with water, and allowing the mass to ferment slightly in a heap, taking care that the fermentation does not proceed too far.

The water used for moistening the logwood should be free from iron or peaty matter, both of which damage the appearance and quality of the wood.

The chips of good logwood gradually become coated over with a green colour, somewhat like that reflected from a beetle's wing.

When the chips are used for dyeing, which is the most common form in which logwood is employed for wool and heavy pieces, they are placed in a bag, made of coarse open material, and hung down into the boiling water, which is intended as a dye-bath, until the colouring matter is extracted; the bags are then removed, and the material to be dyed put in.

Rasped logwood is thrown into the dye-bath along with the material to be dyed."

This method of using logwood in dyeing does not seem nearly so business-like and practical as the method in general use in large establishments for cotton dyeing in Lancashire; the custom there is not to put the logwood into such bags as here described, but to have the logwood finely ground, and then a decoction made of it, either by pouring boiling water upon it in large tanks with a double bottom, or by boiling it for a considerable length of time in closed vessels with water, and sometimes under pressure in what are technically called "wood stills" or "logwood stills." This decoction of logwood does not mark more than say $\frac{1}{2}$ to $\frac{3}{4}$ of a degree on Twaddle's hydrometer. The extracting vessels are placed outside, and it may be a considerable distance from the dye-house, but connected with it by pipes which bring the logwood liquor to a receptacle convenient for the purposes of the dyer, where it is always at hand; the strength is uniform, and instead of taking so many pounds of the wood, he takes so many pails or scopesfull of the liquor. The moistening of the rasped or ground logwood, and even the rasping and grinding of it from the solid wood, is sometimes undertaken by the dyer himself in large establishments; the moistening process intended to soften the wood and perhaps develop the colouring matter, is locally known as "mastering." But a great deal of logwood is supplied by large houses ready ground and moistened, and therefore in a state fit at once to be used either for making decoction or putting into the dye vessel. It is generally considered that logwood does not give results so good when the decoction is made by long boiling or under pressure, as when its colouring matter is extracted by the simple effusion of boiling water upon it; this may, however, be no more than a prejudice. Very dilute logwood extract does not keep well, and is therefore prepared only in such quantities as can be used up within a brief period of time. The following extract shews the methods employed in Yorkshire for dyeing various kinds of black upon wool;—

“Logwood Colours.—A variety of shades of colour can be obtained with logwood alone as the colouring agent, and it enters into the composition of a still greater variety of composite colours. It is essentially a blue colouring matter, and is hence frequently called by the French *bois bleu*. The shade of colour which it imparts to wool is very much modified by the various mordants. Logwood colours are affected by acids which turn them red, and alkalies which change them to blue or purple. By varying the quantity of logwood, various shades of blue are obtained from lavender, with 2 per cent. of logwood, to a dark blue with 30 per cent., which shade becomes very dense and full, when the percentage of logwood is increased to 60 or 70 per cent. The darker of these colours are constantly produced in the dyehouse, both on wool and cloth.

Receipts.—Though dyers' receipts are often instructive in indicating the directions which the dyer may take in order to obtain any given colour or shade of colour, the conditions under which he may work are subject to such a great amount of variation that I deem it necessary, at the outset, to give a word of caution, and to impress upon him the fact that the literal interpretation and carrying out of almost any receipt will produce results alike in the hands of no two dyers, who may happen to be differently circumstanced.

This is readily accounted for, when we consider that the wares may be different in the percentage of colouring matter and tone of colour, the mordants of varying strength, the water often altogether different in quality, the varying dimensions and kind of dyeing vessel used, the different effects of steam and fire heat, and the variations produced by operating on a larger or smaller weight of material. In fact, the varying conditions are so numerous, that dyeing receipts are often illusory on account of the differences which have been enumerated above. The receipts which I shall, therefore, have occasion to give from time to time, I wish to be accepted

with caution, and interpreted with some latitude as to quantities of dye wares, &c.

The receipts are given as typical examples of processes in actual use in the woollen districts, in dyeing goods on the large scale, and are not put forward as the very best modes; these can only be found out according to the different circumstances under which a dyer is placed, and they are often only the result of careful observation and long practice.

The term fast is used in the receipts for a colour which will fairly withstand scouring and milling, but not necessarily the action of light and atmospheric influences. By permanent is meant a colour that will withstand all deteriorating influences both in milling and scouring, and also those to which it may be subjected during a reasonable time of wear. The terms loose and fugitive are applied as opposites to fast and permanent. These definitions are given, not as representing what is frequently attached to them by authors on dyeing, but as those which I wish to be attached to them in these receipts, and which I think may be conveniently applied. The receipts are all given for 100 lb. of wool or cloth, except where otherwise stated.

Common Black at one Operation.

Logwood..... 40 per cent.*

Sulphuric acid..... 0.5 „

Boil half an hour.

Copperas 3 „

Blue vitriol 1 „

Throw on solid or in solution, and boil half an hour longer. Let off and leave over night.

Colour, loose, turning brown in the wear, used for dyeing coloured waste intended for low class goods. Sumac might be used with advantage for a black of this description.

* The percentages given in this and the following receipts are for 100 of wool or woollen fabrics.

This is a loose colour because a good deal of the colouring matter is converted into a lake, and is, therefore, only loosely attached to the fibre. 'The old dyers generally dyed in one bath only, which in part explains the bad results obtained.'*

Common Doeskin Black.

Mordant—

Copperas	3½ per cent.
Blue vitriol	2 „
Alum	2 „
Red argol	3 „
Logwood	3⅓ „

Boil for five minutes, cool down to 100° F. with water, enter the goods, raise to the boil in three quarters of an hour, and boil for an hour and a half. Lift out and leave over night. Some dyers wash off, others leave unwashed.

Dye—

Logwood	24 per cent.
Red argol	1 „

Boil for five minutes, cool down to 180° F. with water, enter the goods, raise to the boil in half an hour, turning by the wince—quickly at first—and boil for another half hour, wind out, cool down over the perch, and wash on the machine with fuller's earth.

If the goods have been manufactured partially from mungos, which often contain cotton threads commonly called burls, it will be necessary to burl-dye them, an operation in which the particles of cotton are dyed black. This operation consists in steeping the cloth in a cistern containing an infusion of a tannin material, commonly sumac or myrabolams, afterwards passing them through a solution of pyrolignite or so-called nitrate of iron (nitro-sulphate of iron). The pieces are then finally washed on the machine with fuller's earth. Colour fast, but not very permanent, becoming brown in the wear.

* Van Laer.

Doeskin Black for Wool.

Camwood 8 per cent.

Boil for fifty minutes. Then add

Bichrome 3 "

Alum..... 1 "

Argol..... 1 "

Boil for fifty minutes, let off, and allow to stand over night.

Dye in—

Logwood 45 per cent.

Fustic 8 "

Sumac 4 "

Boil for one and a half hours; let off. Colour fast and permanent.

This formula contains all the colours necessary to produce a black, namely, red, blue, and yellow. Camwood furnishes the red, logwood the blue, and fustic the yellow. Chromed logwood colours have a tendency to become green, from the production of chromic oxide; the presence of camwood or other red colour makes this change less apparent.

Chrome Black with Blue Reflection (blue through) for Wool.

Mordant—

Bichromate of potash 2 per cent.

Sulphuric acid, D.O.V..... 0.25 "

Boil one and a half hours, and leave over night.

Dye—

Logwood 45 to 55 per cent.

Boil one hour.

If required very clean, as in mixtures of black and white (black and white checks for example), the colour may be fixed more firmly by finally passing it through a warm bath containing 5 per cent. bichromate of potash.

Chrome Black with Violet Reflection (violet through) for Wool.—This is mordanted and dyed as the last. The violet reflection is obtained by using the following

modifier—Single muriate of tin, 1 to 2 pints. Mix the tin spirit in 20 or 30 gallons of water and throw it on the wool, handling up for fifteen minutes.

Chrome Black with Green Reflection for Wool.

Mordant—

Bichromate of potash 2 per cent.

Sulphuric acid '25 „

Boil one and a half hours, and leave over night.

Dye—

Logwood..... 40 per cent.

Fustic 10 „

Boil one hour.

Colour fast and moderately permanent, becoming greener and paler.

Woaded Blacks.—These are the best blacks for either cloth or wool; they are obtained by first dyeing the goods in the indigo vat a light or medium shade, and then dyeing them as for chrome blacks, using less logwood in proportion, as the indigo bottom is more or less dark. Colour fast and permanent.

Lavender on Wool.

Alum 1½

Tartar '25

Logwood 2½

Indigo extract '25

Boil for five minutes, cool to 180° F. with water; enter the goods and boil for one hour. Let off and wash.

Colour moderately fast.”

Mr. Jarmain next treats of the use of cudbear and archil as used in conjunction with logwood, in order to give a desired hue or bloom to the colour; they are said to be used as a “bottom” or “ground,” but perhaps considering the small proportion applied along with the logwood, and the qualities they communicate to the colour, the expression “topping,” which is frequently used for this class of admixture, is more appropriate and correct.

"These colours are employed largely as a bottom or ground for indigo on wool and cloth, and also as before stated, for many mixed or composite colours, but the colours are somewhat fugitive.

The mordants affect the shade of colour only to a small extent; in fact, they may be employed without mordant. They are most affected by a mordant of tin, chiefly through the influence of the free acid contained in the tin spirit, which, like all other acids, reddens and brightens the colour, changing it to a maroon. The weed colours, as they are called, are mostly used for the purpose of modifying and blooming other colours, but as they are fugitive, the bloom soon passes away. Their brightness and beauty, however, render them exceedingly well adapted for the colours required for ladies' wear.

The following formula is given as an illustration of the use of cudbear along with logwood:—

Logwood Blue for Wool.

Mordant—

Bichromate of potash	1 per cent.
Alum	3 "
Tartar.....	1½ "

Boil for one and a half hours, let off, and leave over night.

Dye—

Logwood	20 per cent.
Cudbear	1 "

Boil for one hour, then throw on 20 quarts single muriate of tin, diluted with 20 or 30 gallons of water. Handle up for fifteen minutes, let off, and wash. Colour moderately fast."

Upon the red woods and their use in wool dyeing we have the following:—

"These important dye wares comprise two classes:—

1. Red woods, whose colouring matters are freely soluble in boiling water; these include Brazil-wood, Lima-wood,

Santa Martha, or peach-wood ; Sapan-wood, and Pernambuco-wood. 2. Red woods, which are almost insoluble even in boiling water ; these include camwood, barwood, and sanders-wood, and caliatour.

The first class is imported in the form of blocks or billets from Central and South America, and the West Indies, and is sold to the woollen dyer in the powdered state. They are said to contain the same colouring principle, called by Chevreul, who first obtained it, by the name of brazilin ; it can be obtained in needle-shaped crystals, which are nearly colourless, and have a bitter-sweet taste. By oxidation it is transformed into brazilëin, by a change which is analogous to that which takes place when indigo white becomes indigo blue, and when hæmatoxylin becomes hæmatëin.

I find that peachwood is almost the only wood of this class which is employed in wool dyeing, and that only to a limited extent ; it is never used as a self colour, its chief employment being for the purpose of imparting a purple tone to other colouring matters.

The second class, embracing camwood, barwood, sanders-wood, and caliatour, is very important to the woollen dyer. They are the produce of several species of *Pterocarpus*, which grow in tropical countries, and are imported into this country in the form of knotty billets or blocks, which are prepared by rasping for the use of the dyer ; the wood, on account of the very slight solubility of its colouring matter, is generally boiled in contact with the article to be dyed. The colours which they impart to wool are red, or red-brown, with a mordant of tin, alum, or bichrome, the colour being of a dull shade when copperas is used ; the colours are very permanent and fast, and are on that account much employed in the dyeing of wool and woollen cloths, which have to be scoured and milled.

The colouring matter seems to be the same in all ; there is a colourless principle called santal, which by oxidation is transformed into the red colouring matter,

santalin, by a reaction analogous to those which take place in the colouring matters of indigo, logwood, and peachwood.

These [woods are seldom or never used alone as a colouring matter for wool, their principal employment being to give the requisite red tone to browns, clarets, violets, maroons, blacks, and other colours which contain a red in their composition; they are also the best bottoms for indigo which can be put on, being much faster and more permanent than a bottom obtained with archil or cudbear.

Claret Brown on Wool.

Mordant—

Bichromate of potash $1\frac{1}{2}$ per cent.
Sulphuric acid 0.25 „

Boil for one hour, leave over night.

Dye—

Camwood 34 „
Barwood..... 10 „
Logwood 2 „
Cudbear 1 „

Boil for two hours, let off.

The shade may be considerably darkened by the addition of copperas towards the end of the operation.”

Upon madder Mr. Jarmin has not much to say, since it is but little employed in wool dyeing. He says that he is not aware that artificial alizarine is in use in the woollen districts; it appears to be used to some extent on the continent, if we may judge from several receipts which have been published for its application in French and German journals. The following is given as one of the cases in which madder forms an important constituent of the colouring matter:—

“In wool dyeing the chief uses of madder, besides acting as a ferment in the indigo vat, are for the production of drabs, browns, and olives, for which its colouring matters are well adapted. The colours obtained with madder on wool are very fast and permanent.

Brown on Wool.

Mordant—

Bichromate of potash 1 per cent.
 Sulphuric acid (D.O.V.) 0.5 „

Boil one hour, let off, and leave over night.

Dye—

Madder 11 „
 Logwood 1 „
 Camwood 8 „
 Fustic 10 „

Boil for two hours. Colour fast and permanent.”

The important yellow colouring stuff fustic, and its uses in conjunction with various red woods to obtain shades of brown, are ably treated of by the lecturer; his audience had the advantage of inspecting illustrations of the samples dyed with various mixtures. The reader will, however, be able to obtain an intelligible idea of the subject from the following extract:—

“Fustic is the wood of a tree called *Morus tinctoria*. It is imported chiefly from Central America and the West Indies. It is known to the dyer under the names of old fustic and yellow wood. It is prepared for the use of the dyer as chipped fustic, rasped fustic, fustic extract. It is used extensively in all three forms. When the chips are used they are placed in a bag in the boiling water, in the same way as that in which logwood is used. Rasped fustic may be thrown into the pan along with the goods to be dyed.

The tinctorial principles contained in fustic consist of moritannic acid, a pale yellow crystallisable substance, freely soluble in water, morin or moric acid, a crystallisable substance nearly insoluble in water. As moric acid is but slightly soluble even in boiling water, the moritannic acid is the principal available colouring agent in fustic. Fustic gives a yellow colour on wool which has been mordanted with chloride of tin, alum, or bichromate

of potash, and olive green with a mordant of sulphate of copper or copperas. Fustic is rarely or never used as a self colour, but it is very extensively employed along with logwood and the red woods in producing that infinite variety of shades of composite colours known as blacks, browns, olives, drabs, &c., for which it is eminently adapted. Dyed on wool, with a bichromate of potash or copperas mordant, it produces a fast and beautiful and permanent colour.

In the heavy woollen cloth districts, where pilots, beavers, naps, reversibles, fancy trouserings, and such like goods are manufactured, it is more extensively used than any other yellow dye-ware.

Its use and modifying action on other colours, such as logwood and the red woods, are best studied by dyeing equal weights of mordanted wool or cloth with varying quantities of fustic, and of the woods I have just named.

As a rule, the different shades of brown are obtained by using more than one red colour, and sometimes three or four of the red colours are required in order to produce shades exactly like a given pattern. In my opinion there is no department of dyeing which requires such an amount of skill, and practical experience, and knowledge of the modifying action of colours upon one another, as in the dyeing of the different tones of blacks, browns, and drabs, and it is wonderful to see with what precision some of our practical dyers can arrive at any particular tone or shade.

In the use of the red woods as modifying agents, the following points should be borne in mind :—

1. Camwood is stronger, faster, and brighter than either barwood or sanders.
2. Barwood gives brightness and lustre, but lacks body.
3. Sanders-wood gives a more yellow red than camwood or barwood. It contains more colour than barwood, but its colour is not so bright.

4. Madder gives the finest, brightest, and fastest colour ; it contains more yellow colour than the red woods, but its red colouring matter is superior to those of the red woods.

5. Sumac gives a fine olive yellow shade to brown, and helps to sadden when copperas is used.

6. Logwood in small quantities, say one, two, or three per cent., saddens or dulls the colours of the red and yellow woods.

7. Cudbear has a brightening effect, giving a purple tone to colours.

Incidentally, I may mention a particular effect which is frequently met with in dyeing of wool. The tips of the locks of wool often take a deeper shade of colour than the remaining portion of the lock, and as the wool becomes thoroughly mingled in the processes of carding, scribbling, and spinning, to which it has to be subjected preparatory to its final manufacture into cloth, the dyer has to take into account the effect which will be produced by such admixture of colour.

In cases of this kind, the general effect produced by the dye may be ascertained by teasing out in the hand a small sample, so that the whole is made as even as possible. On comparing this with the pattern, it will be seen whether the proper effect has been obtained, or whether some additional colour, and what colour, is required.

There is another effect which is often perplexing to a young dyer ; the red and yellow colours have different affinities for the mordanted wool ; the red wood colours partially displace the yellow colours. If wool, in the course of dyeing, appears to have received a sufficient amount of yellow, but there is a deficiency of red, and the dyer proceeds to add what he conceives to be a sufficient quantity of red to make up the deficiency, and bring the goods up to sample, he will frequently find that he will then have on too much red and too little yellow. The additional quantities of wood required are

added in the form of rasped or ground wood, which is well worked up with the goods, or a solution of the extract may be employed for the same purpose.

The following receipts are examples of the use of several woods which were found to be required in order that a particular shade of colour might be obtained :—

Tan Brown.

Mordant—

Bichromate of potash 1 per cent.

Boiled for one hour.

Dye—

Madder 3·2 per cent.

Fustic 4·8 ,,

Camwood 2' ,,

Barwood 1·75 ,,

Sumac 2·1 ,,

Boiled two hours.

Tan Brown, redder shade.

Mordant—

Bichromate of potash 1 per cent.

Boil one hour.

Dye—

Fustic 7·2 per cent.

Madder 4·8 ,,

Camwood 2·8 ,,

Sumac 2·4 ,,

Boil two hours.

California.

Mordant—

Alum 1 per cent.

Bichrome 1 ,,

D.O.V. $\frac{1}{3}$,,

Boil one hour.

Dye—

Fustic 25 per cent.

Madder 2 ,,

Camwood 3 ,,

Boil one hour and a half.

Dark Drab.

Dye—

Camwood	6·5 per cent.
Sumac	2' "
Madder	2·5 "
Fustic	4' "
Logwood.....	2·5 "

Boil one hour and a half. Sadden with 1 per cent. copperas.

Olive Drab.

Mordant—

Bichromate of potash	1 per cent.
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Boil one hour.

Dye—

Fustic	10' per cent.
Sumac	2' "
Madder	5' "
Logwood.....	'2 "

Boil two hours.

Madder Brown.

Mordant—

Bichromate of potash	1 per cent.
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Boil one hour.

Dye—

Fustic	22·7 per cent.
Madder	11·35 "
Logwood.....	1·13 "

Boil two hours.

Drab.

Dye—

Fustic	1·7 per cent.
Madder	4' "
Cudbear	'1 "
Sumac	'8 "

Boil one hour and a half, and sadden with '2 per cent. copperas.

Quercitron bark, we are told, may be used for the same purposes as fustic, but it does not give an equal body of colour, and is not so extensively employed.

Flavin, which is a concentrated extract of quercitron bark, being about sixteen times as strong, is often used when brighter shades are required than can be obtained from either fustic or bark ; it is used as the yellow part of scarlets and oranges, and for almost any colour where a bright yellow part is wanted.

Young fustic (*Rhus cotinus*), is also very suitable for using with cochineal in the dyeing of scarlets and oranges.

Upon turmeric, Persian berries, and sumac, we have the following :—

Turmeric.—In wool dyeing, the use of turmeric is confined to the dyeing of a certain class of browns on stuffs, and is often associated with colours of a fugitive character like itself. It finds no use in the heavy cloth districts, and if its employment were altogether discontinued as a woollen dye material, it would be no great loss to the public who happen to have to wear goods dyed with it.

Persian Berries.—In wool dyeing Persian berries find no use in the heavy woollen trade, the colour which they give to mordanted wool not being [sufficiently fast to withstand milling and scouring processes. It is, however, often employed as a yellow dye for goods for ladies' wear, such as scarlets and oranges.

Sumac.—This astringent substance is of considerable importance in the dyeing of certain drabs and browns on woollen goods, as, in addition to the tannin which it contains, there is also a yellow colouring matter which has not yet been studied, but which performs an important part in the production of browns and drabs.

Its action on wool mordanted with bichrome is to produce a fine olive yellow ; with a mordant of tin, a bright yellow ; and with one of copperas, a dark slate. This last effect is owing to the action of the tannin in the sumac upon the salt of iron.

The chief use of sumac to the woollen dyer, however, is for the purpose of dyeing cotton or vegetable matter which may happen to be mixed up with wool.

1. In the form of burls, or threads, or seeds.
2. In union or mixed goods, in which there is a cotton warp with a woollen weft.

The goods, after having been dyed in the ordinary way, as for wool, are steeped in a decoction of sumac in the cold, and then a solution of so-called nitrate of iron, or of pyrolignite of iron, if the colour is black ; but for the red wood, yellow wood, and aniline colours, the goods which have been steeped in sumac decoction are transferred to a solution of oxymuriate of tin of 2° or 3° Tw.

A tannate of tin is probably formed in this operation, which enables the cotton to take up dyes in the same manner as wool."

Upon wool dyeing with cochineal and lac dye we extract the following :—

Cochineal.—On wool its chief use is for the production of scarlets, oranges, and crimsons, rose pinks, and such like colours, flannels and serges being the goods mostly dyed with cochineal colours.

The yellow portion of the scarlets is obtained by using flavin, which is the best for the purpose ; or young fustic, which answers very fairly ; and lastly Persian berries are sometimes used, but the yellow colour obtained with them is not fast.

The mordant used in dyeing scarlets is a salt of tin along with tartar. There is a great diversity of practice among the dyers in the use of tin spirits in scarlet dyeing. Some use the ordinary double muriate or single muriate, others the muriate to which is added one or two per cent of oxalic acid ; some again use a nitrate of tin or a sulphomuriate. I do not know that any special preference should be given to any particular tin spirit, for I have seen equally good results with all of them. When the single muriate will answer, it seems to me unnecessary that the operation should be complicated by the use of a more complex mixture.

When goods are hard woven, a tin spirit which

contains but little free acid does not answer well. The colour is deposited too much on the surface of the cloth, and the centre is often not dyed at all. A tin solution which contains a good deal of free acid, however, enables the colour to penetrate better into the centre of the cloth, because the coloured lake which is formed by the combination of the carminic acid with the oxide of tin is kept longer in solution by the free acid.

The penetration of the colour into the centre of the cloth may often be accomplished by entering the goods at a temperature below the boil, and heating the bath up to the boiling point very gradually.

A proportion of tartar greater than 4 per cent. of the woollen material to be dyed has the effect of yellowing the shade of scarlet, the yellowing being in proportion to the excess of tartar.

An increase of the tin mordant, the other materials remaining the same, has the effect of intensifying the shade of colour without sensibly increasing the yellow.

In dyeing scarlets and oranges with cochineal, the mordanting and dyeing are done in the same bath, kept at a boil for an hour or an hour and a half; wood cisterns being generally employed for the bath, and the boiling is done by perforated steam pipes."

Lac Dye.—The identity of the colouring matter of lac dye with that of cochineal has not been fully established, but there is a great similarity in their action on mordanted wool, the chief difference being in the tone and intensity, or depth of colour. Lac-dyed colours are also somewhat faster and more permanent than those of cochineal.

Lac dye is imported in the form of hard cakes, which are ground to a fine powder for the use of the dyer. The dyer works up the powdered colour into a paste, with a mixture of hydrochloric acid and his tin spirit, and then adds it to the dye-bath, along with the goods to be dyed; the dyeing is then performed exactly in the same manner as with cochineal.

In practice it is found to be advantageous to combine the brightness of the colour of cochineal with the solidity and permanency of lac dye; this is done by dyeing the goods first in a bath of lac dye, and then in a separate bath with cochineal, washing out from the first bath before entering it in the second.

The following are the proportions and cost of dyeing goods on the large scale by this process :—

Scarlet.

For 100 lb. of cloth :—	s.
Lac (mixed, varying from 1s. 6d. to 6d. per lb.), average 1s.	8·08
Cochineal 2s. per lb.	6·00
Argol (110s. per cwt.), 1s. lb.....	5·
Tin spirit of 45° Twaddell } as stannous chloride } 1¼ d. per lb.	2·4
Flavine at 2s. 6d. per lb.....	·08
Cost of materials for woollen cloth...	21·56"

Upon the use of ammoniacal cochineal and the new artificial colouring matter eosine, Mr. Jarman communicates the following particulars:—

“Ammoniacal Cochineal.”—When cochineal is ground and worked up into a paste with strong ammonia, say 16° of the ammonia gauge, the colouring matter becomes transformed into a new colour called carminamide.

This colour does not produce red or scarlets, but is employed along with cochineal for the production of rose pinks, crimsons, and such like colours.

The mordant which works best with ammoniacal cochineal is the nitrate of tin.

The following are the proportions used on the large scale for the production of a rose pink :—

For 150 lb. cloth :—
1½ lb. ground cochineal, made into a paste with 1½ pts. ammonia 16°, and left overnight.
2½ lb. ground cochineal.

1 $\frac{1}{4}$ lb. tin dissolved in 13 lb. nitric acid.

5 lb. argol.

Boil one hour."

"*Eosine*.—A new dye known under the name of Eosine has recently been added to the list of red dyes, and as it is likely to become a competitor in the production of scarlets on wool, I have thought it advisable to give a short account of it here.

The word 'Eosine' signifies day-dawn, implying that the colour is that of the rosy hue of morning. On silk, the colour is that of the rose, but on wool it is scarlet.

In order to produce it, a substance called resorcin, obtainable from a variety of sources, is treated with phthalic acid, whereby a new and fine yellow colouring matter is produced, called fluorescine, on account of its possessing the property of fluorescence in a marked degree. This new body, when treated with bromine, gives the colour in question, eosine, which is a bromine of fluorescine. Eosine also possesses fluorescent properties, which you will readily see, as I pour the eosine solution into this tall cylinder of water, and illuminate it with the magnesium light.

Woollen goods are dyed with eosine, using alum as a mordant in the same bath.

The goods are boiled for a few minutes with 8 per cent. of alum, and the dye in solution is then introduced at intervals, until the requisite depth of shade is obtained.

The dye will bear soap washing fairly, but will not stand severe milling. It dyes readily along with aniline and other colours, and promises to be a very useful addition to our present list of dye wares."

In the sixth lecture, Mr. Jarman treats of aniline colours. We omit the historical remarks and chemical formulæ explaining the production of these colours, as being either familiar to our readers or easily accessible in other works which go more at length into these subjects; the practical information contained in the following extracts is at least

useful as indicating the present method of operating with these colouring matters, and may be compared with what has appeared in previous numbers of this journal upon the same subject.

“Dyeing Operations with Aniline Colours.”—Wool has such a powerful affinity for the aniline colours, that the chief difficulty in dyeing with them is to obtain even work. This is accomplished in a variety of ways:—

1. The goods are introduced quickly at a temperature much below the boil, the bath is then heated up very gradually for half an hour, the goods being kept in constant motion all the time.

2. Where the goods can be entirely removed from the bath, it is found advantageous to introduce the whole amount of colour at two or three separate times.

3. Evenness may frequently be obtained, by the addition to a large bath of a few buckets full of crystals of sulphate of soda.

4. The goods must be well scoured, and free from every trace of grease, and soft water should be used. Wool requires no mordants for the aniline colours; the so-called mordants required in dyeing with some of them merely act the part of a modifier, and are in no sense mordants in the proper meaning of the term.

Aniline colours, therefore, behave to wool as substantive colours.

The aniline colours are neither mill-fast nor sun and weather proof; I cannot, therefore, classify these among the fast and permanent colours which I have already described; they, however, vary very much in fastness and permanency; some of the blues will withstand a good deal of severe treatment. They serve an important purpose exceedingly well, in furnishing bright and brilliant colours, of every conceivable shade, for goods which are not required to be exposed to deteriorating influences; but they far surpass the fast colour in beauty. It is not surprising, therefore, that the gentler portion of humanity should delight themselves and us, by adorning

themselves with these glorious colours, which rival the tints of the rainbow, the rosy hue of morning, and the beautiful colours of the winged tribes of the sunny south.

Roseine, or the acetate, is prepared for dyeing operations by dissolving it in boiling water, and filtering the solution through flannel, so that no undissolved small particles of the dye can come in contact with the goods to be died; the solution is then added to the bath as required.

Magenta, or the hydrochlorate, is got into solution by dissolving it in boiling water, in the proportion of 2 gallons of water to every ounce of the dye, but a concentrated solution may be made by dissolving the colour in methylated spirit and then adding boiling water. If the crystals be worked up into a paste with glycerine, before treatment with water, a very perfect solution is obtained.

Ponceau.—Ponceau is another aniline red, which may be classed with magenta and roseine. It is, however, a more pure red than either, and is considered a faster colour. The process of its manufacture has not been made public. Its solution is prepared and used by the dyer in the same manner as that of roseine.

There is also an aniline scarlet, but it does not produce a scarlet on wool equal to what can be got by other means.

Aniline Crimson.—This is a crude, common magenta, often called claret-paste, which is exceedingly useful for dyeing clarets, maroons, and any composite colour containing magenta. The colour is prepared for dyeing by dissolving it in hydrochloric acid, then adding boiling water, and filtering. Any excess of acid may be corrected in the dye-bath by an alkali.

With aniline violet the same process of dyeing is followed as with red. "The well cleansed goods are entered at about 130° F., and well handled; the bath is gradually heated up to near the boiling point. The colour is introduced at two or three times. For the bluer shades of violets it is found to be

advantageous to make the bath slightly acid with sulphuric acid, which has a tendency to develop the blue colour."

The methods of dyeing with Nicholson's blue and other of the aniline colours are given as follows:—

"*Nicholson's Aniline Blue*.—The dyeing of wool is performed in the following manner:—

A solution of the colour in boiling water is made and added to the dye-bath, made alkaline with silicate of soda or borax. The goods are then washed out and passed into a bath of water acidulated with sulphuric acid. The acid converts the soluble sodium salt, which is of a bluish grey tint, into the insoluble acid, which is blue. If the goods are required to be dyed up to pattern, portions of the piece are torn off from time to time, washed, and then put into the acid bath, and more colour is added to the alkaline bath if necessary and the dyeing operation continued."

"*Aniline Greens*.—There are several greens in use by the dyer. The colour called iodine green is, however, I think, preferred.

The dyeing with iodine green is done in a bath of silicate of soda, as with the alkali blues; the colour is afterwards developed in acid, or, better still, in tin spirit, which gives a faster colour.

The proper shade of green is often arrived at by the addition to the bath of the necessary quantity of picric acid."

"*Picric Acid*.—Picric acid dyes wool a bright yellow, with a slight green tinge, which is rather objectionable. It is much employed to produce greens along with extracts of indigo, and to modify the shades of reds and browns; in fact, it serves the same purpose with the aniline colours that the yellow woods do with the red woods, in modifying their shades.

The dyeing of wool with picric acid presents no difficulty. The dye is freely soluble in water. It is very advantageous to make the bath acid with sulphuric acid."

"Aniline Browns.—Bismarck Brown.—These are an extremely useful class of colours. They dye wool easily, and their shades are generally modified to the red side by the use of magenta; to the yellow side by picric acid, Persian berries, or turmeric acid; and to the blue by extract of indigo. There are several modes of preparing these browns; one of the most commonly used colours is prepared by acting on dinitro-benzol with granulated tin and hydrochloric acid, which produces phenylene diamine, which is then acted on by an alkaline nitrite.

The solution of the colour is prepared for the dyeing operations by dissolving it in hydrochloric acid, and diluting with hot water. The dye is then ready for use."

Upon aniline black, as applied to wool dyeing, we have nothing of any value, the difficulties in the way are not yet overcome. The vanadium method is mentioned, but not as being applied on the large scale.

The lectures conclude the practical part with some remarks upon dyeing mixed fabrics, which we extract. Mr. Jarmain finishes by expressing his surprise and regret that there should be so little connection between the dyers and chemical knowledge. We give his remarks, which are an echo and a repetition of what was expressed one hundred and twenty years ago by Dr. Home, and eighty years ago by Dr. Henry, and many a time since by men as able as they were, but with very little useful result. The time has not yet come, though it seems to be dawning, when practical men in England will care greatly to have recourse to science, so long as they can get on in some way or other without it. If we have not lost much so far by the common disdain of science, it seems clear that things are wearing a different aspect now; a more effective competition has sprung up abroad, and it is becoming impressed upon our manufacturers that in the future they may want all the help they can get to maintain their position.

"Dyeing of Mixed Fabrics of Cotton and Wool.—Blues.—Dye the wool or worsted first with an alkaline

blue, in the ordinary way, with silicate of soda, taking care that the wool is dyed a little lighter in shade than the pattern, as in dyeing the cotton, afterwards the wool takes up a little additional colour. After dyeing the wool, wash out and develop in acid, and wash again; then dye the cotton blue up to shade, adding the colour until the proper shade is obtained. A solution of alum should be used along with the cotton dye. The cotton is dyed in a cold bath.

With the other aniline colours, after the wool or worsted has been dyed in the ordinary way, with the precaution of leaving it a little under shade, for the reason stated under blues, the cotton is prepared for receiving the dye by washing it out from the wool dye-bath, then steeping the goods in sumac liquor, and afterwards in a solution of oxymuriate of tin, of about 3° Tw. for an hour. The cotton so prepared may be dyed up to shade in the cold with the same dye as that used for the wool. In this manner magenta, the Hofmann and Paris violets, and the iodine greens, may be dyed on mixed fabrics.

The aniline colours are frequently employed as a topping to other colours which, though fast and solid, lack brilliancy.

Time forbids me to enter more lengthily into the industrial application of these extraordinary colours which, since their introduction just twenty years ago, have completely revolutionised the dyer's art in one branch of his work. They form a separate series of tinctorial substances, which enable the dyer to obtain every shade of colour previously obtained by other agents, and though wanting in solidity and permanency, they supply such abundant opportunity for the dyer to produce colours much in demand, they will always find a place in the dye-house.

I cannot bring these lectures to a conclusion without expressing regret that the principles of the dyer's art should have been so much neglected in this country, and

that our woollen manufacturers should have so long submitted to have such a very important branch of their manufactures carried out by men who for the most part worked by purely rule of thumb processes. When I say this, I do not wish to imply that the dyer is not a skilful workman, for, considering his opportunities, he has brought his art to a wonderful state of perfection. But where such large interests are involved as they are in the woollen manufactures of the United Kingdom, it seems strange that the manufacturers have not yet opened their eyes to the fact that, in this scientific age, we can no more hope to compete with those who work out their processes on scientific principles, than we could hope to overcome an enemy armed with modern weapons of precision if our soldiers were dependent upon the old "Brown Bess" of former times. So far as I know, the Society of Arts' scheme of offering prizes to students in dyeing, after examination, is the first attempt which has been made in this country to induce young dyers to study their art; but it is a deplorable fact that, throughout the length and breadth of this land last year, there was found only one student who ventured to offer himself for examination in wool dyeing. If our manufacturers studied their best interests, they would at once set about offering inducements to their young dyers to make themselves better acquainted with the principles of their art, by providing a library of the best standard works on dyeing for their dye-house, by furnishing a small laboratory for their works, by encouraging their young men to study chemistry, by encouraging the formation of dyers' societies in their district, and by uniting to endow chairs in colleges now in existence devoted to technical education. By such means, or others of a similar character, we might hope in time to have a class of working dyers proud of their art, skilful in the practice of it, and able to compete with the dyers of any other nation.

My best thanks are due to several woollen manufacturers and dyers in West Yorkshire who have given

me the privilege of visiting their dye-houses, and have explained their processes to me. I have no permission, however, to mention their names."

5. *Aniline Black in Court in America.*

IN 1872, Mr. J. Muller Pack, the proprietor of Lightfoot's American patent, brought an action against the Merrimac Manufacturing Company to restrain them from using or making aniline black by this patented process. The action has only lately been tried and decided in favour of the holder of the patent. The following account of the trial is condensed from the *American Chemist* of July last. The defendant Company pleaded that they did not use Lightfoot's patent process, but that they produced aniline black by means of a similar composition, but without copper salts, and that as far as regards this aniline black, Lightfoot's patent was covered and anticipated by the patent to Calvert, Lowe, and Cliff, taken out in 1860, some three years before Lightfoot's patent.

The process of Calvert, Lowe, and Cliff consisted in printing on calico prepared with chlorate of potash a solution of muriate of aniline; a colour called emeraldine was thus produced which was very dark green, nearly black. The defendants stated that they used a modification of this process. Instead of preparing the cloth with chlorate of potash, they printed a thickened mixture of chlorate and muriate of aniline, which are substantially the same ingredients as in Lightfoot's patent, but they did not use copper, which was held to be the distinguishing feature of Lightfoot's patent. The question then turned upon the truth of this denial of the use of copper.

Numerous analyses were brought forward of the aniline black goods manufactured by the Merrimac Manufacturing Company, and of the compositions they employed in printing the black, and all were declared to contain copper. On the other hand, the primary materials used in the composition of

the colour were free from any trace of this metal. The presence of copper in the coloured pieces could only then be attributed to the vessels and utensils employed in preparing the colour, and the experts, upon inspecting the process, were soon convinced that this was the case. One of them states that the chlorate and muriate of aniline were in the first instance ladled out with copper scopes which shewed evidences of corrosion; the pans, in which the colour was boiled in thickening, were made of copper and exposed a large surface to the action of the acid solutions; the agitator which mixed the colour was made of copper; copper was the material of the paddles used to transfer the colour to copper colour boxes, in order to be printed by a copper roller with a doctor containing copper; and it is intimated that, if it were possible, copper printers and back-tenters would have been employed.

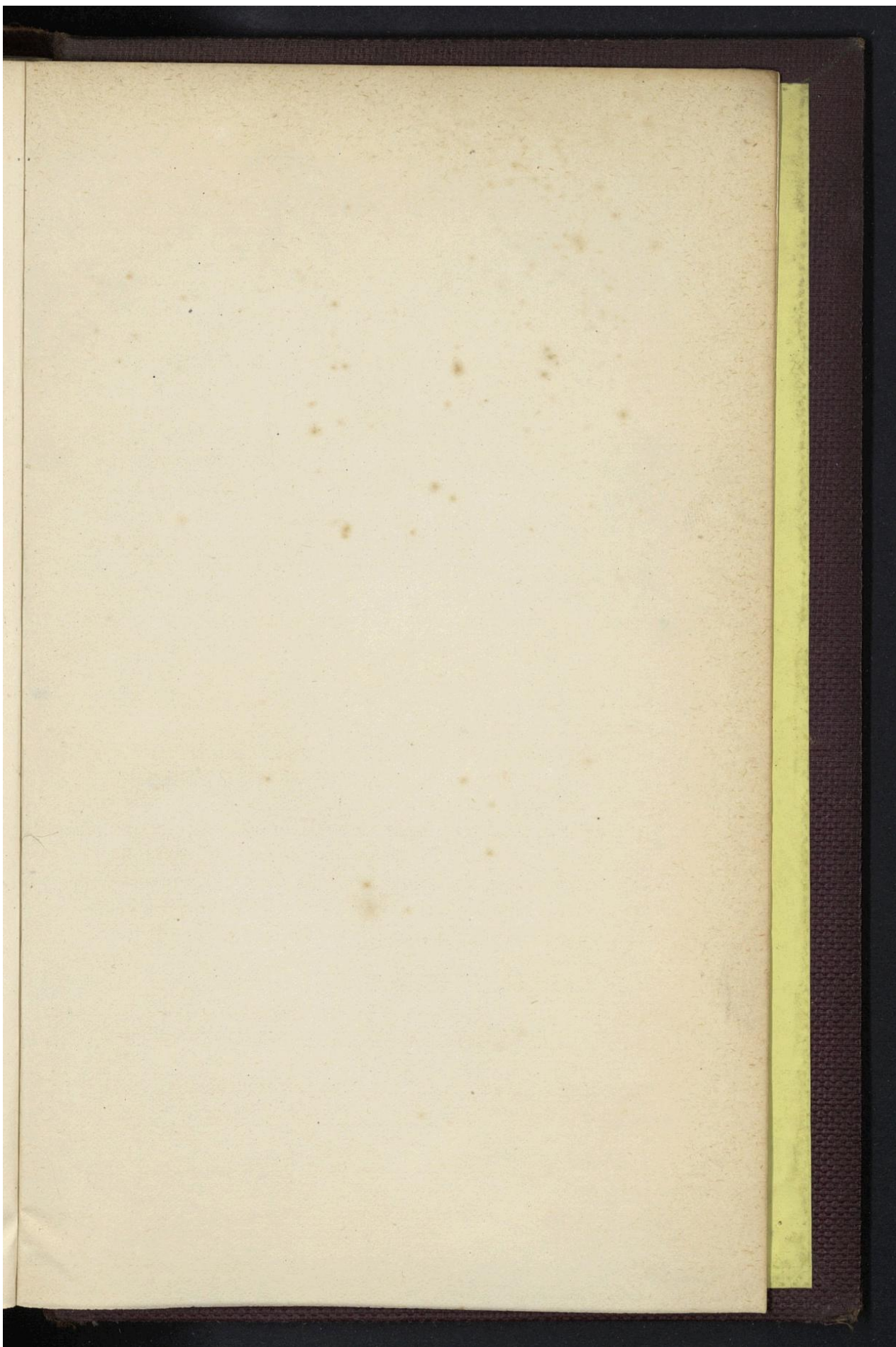
Under these conditions, sufficient copper was dissolved in the colour to make it similar to Lightfoot's, and to give colours of the same quality. By making use of the same materials, but avoiding the use of copper vessels and rollers, it was proved that good blacks could not be obtained unless a copper salt was added.

The defendants then stated that they could obtain blacks without copper by using a higher temperature than ordinary in the ageing, but it was proved that the use of high temperatures with acid salts of aniline resulted in a weakening of the fibre by corrosion, which amounted to 26 and as high as 47 per cent., while the colour made by Lightfoot's process, or the process actually employed by the Merrimac Company with their copper utensils, did not sensibly weaken the fibre.

It was finally decided by the tribunal that the process of making aniline black, as used by the Merrimac Company, was identical with Lightfoot's process, and that the apparently accidental manner in which the copper got into the colour did not prevent the process being an infringement of Lightfoot's patent; and, further, that the previous patent quoted did not invalidate Lightfoot's.

Palmer and Howe, Printers, Bond Street, Manchester.





THE LIGHTFOOT CASE

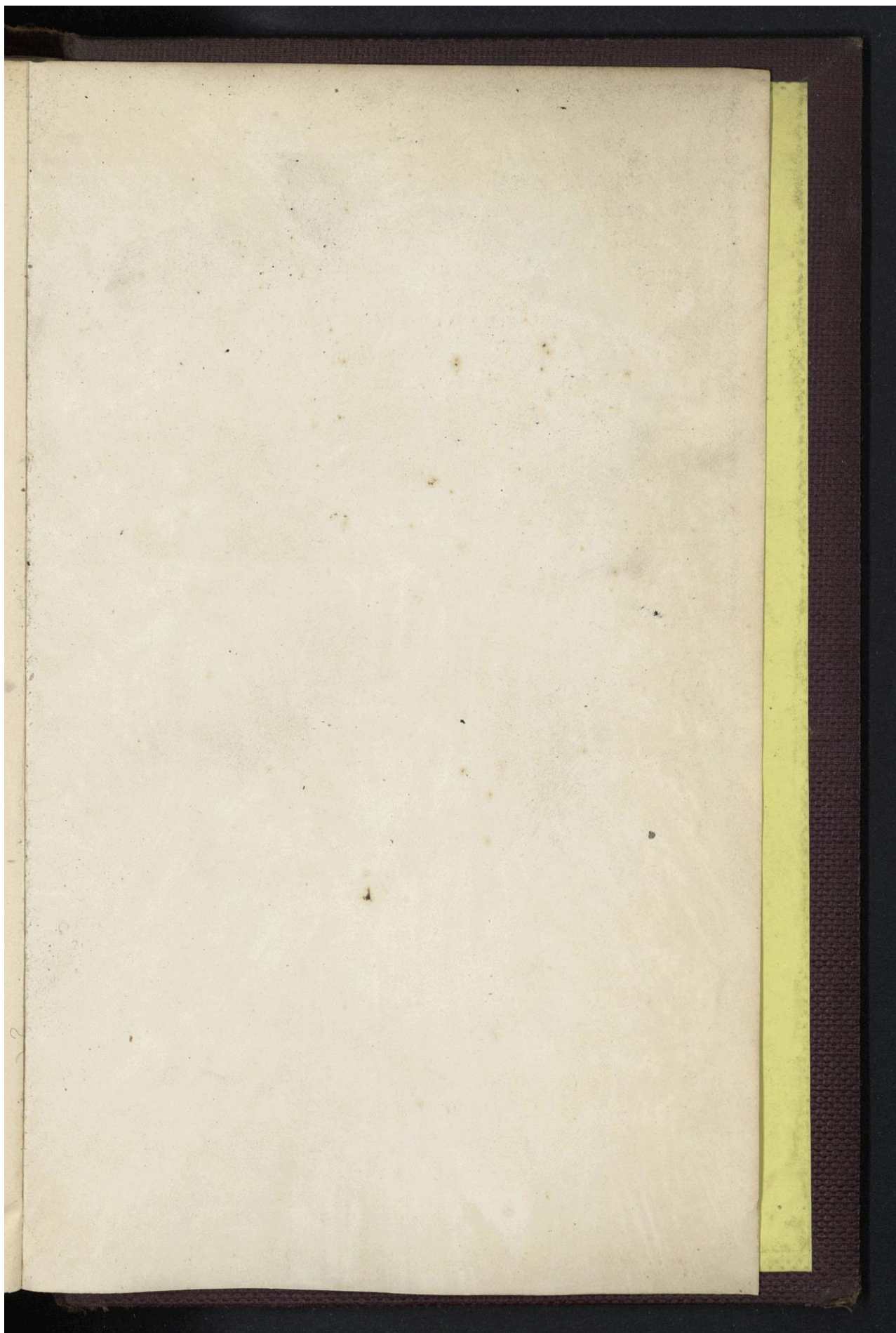
... were free from any ... The ... in the ... and ... in the vessels and ... the ... and the experts ... the ... that this was the case. One of these ... the ... and ... of ... in the ... which showed evidence ... the ... in which the colour was boiled in ... were made of copper and exposed a large surface ... of the acid solution; the ... which ... was made of copper; copper was the material of ... used to transfer the colour to copper colour boxes ... by a copper roller with a doctor ... it is intimated that if it were possible, copper printers and back-tenters would have been employed.

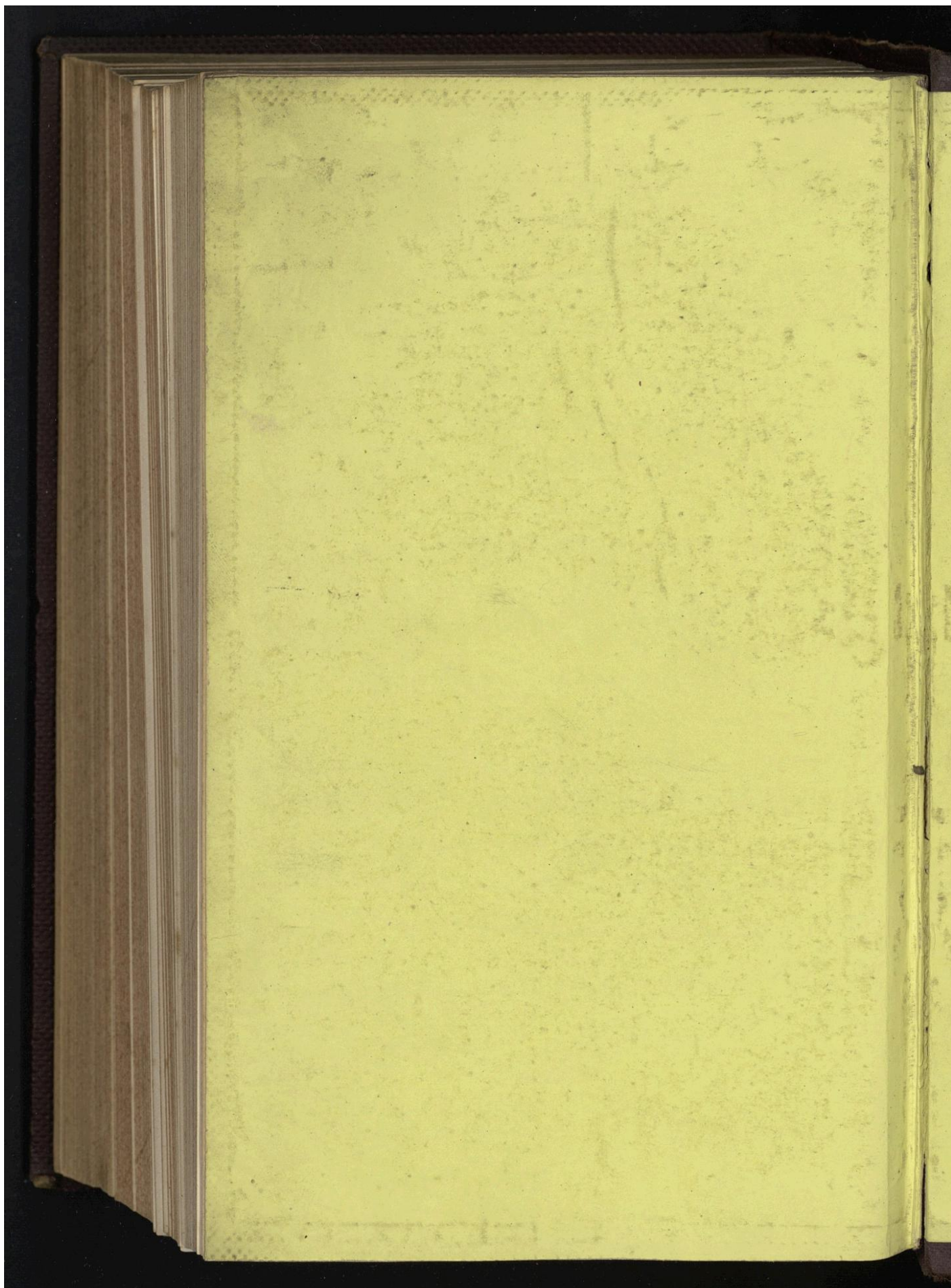
Under these conditions, sufficient copper was dissolved in the colour to make it similar to Lightfoot's, and to give colours of the same quality. No staining or of the same ... but ... rollers. It was proved that good ... a copper salt was added.

The defendants then stated that they also were able to make ... without copper by using a higher temperature ... in the ageing, but it was proved that the use of high temperatures with acid salts of alkalis resulted in a weakening of the ... which amounted to as high as 50 per cent, while the colour made by Lightfoot's process, or the process actually employed by the Maritime Company with their copper atensile, was ... the fibre.

It was finally decided by the tribunal that the process of making aniline black, as used by the Maritime Company, was identical with Lightfoot's process, and that the apparently accidental manner in which the copper got into the colour did not prevent the process being an infringement of Lightfoot's patent; and further, that the ... did not invalidate Lightfoot's.

... ..





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