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NOTICE BIBLIOGRAPHIQUE

Auteur(s)	Crace-Calvert, Frederick (1819-1873)
Titre	On improvements and progress in dyeing & calico printing since 1851 : illustrated with numerous specimens of printed and dyed fabrics
Adresse	Manchester : Dunnill, Palmer, & Co. ; London : Trübner, [1862 ?]
Collation	1 vol. (28 p.) : échantillons ; 22 cm
Nombre de vues	28
Cote	CNAM-BIB 4 Ke 73 (5)
Sujet(s)	Impression sur étoffes -- Innovations technologiques -- 19e siècle Teinture -- Innovations technologiques -- 19e siècle
Thématique(s)	Matériaux
Typologie	Ouvrage
Note	La partie supérieure de la page de titre contenant le début du titre est manquante. - Publié vers 1862 d'après la bibliographie
Langue	Anglais
Date de mise en ligne	05/02/2026
Date de génération du PDF	07/02/2026
Recherche plein texte	Disponible
Notice complète	http://www.sudoc.fr/124234577
Permalien	https://cnum.cnam.fr/redir?4KE73.5

H^o Re 43 (5)

IMPROVEMENTS AND PROGRESS
IN
DYEING & CALICO PRINTING
SINCE 1851.

ILLUSTRATED WITH NUMEROUS SPECIMENS OF
PRINTED AND DYED FABRICS.

BY

DR. F. CRACE CALVERT, F.R.S., F.C.S.,

*Professor of Chemistry at the Royal Institution, Manchester; Corresponding Member
of the Royal Academies of Turin and Rouen; of the Pharmaceutical
Society of Paris; Société Industrielle de Mulhouse, &c.*

A LECTURE DELIVERED BEFORE THE SOCIETY OF ARTS.

REVISED AND ENLARGED BY THE AUTHOR.

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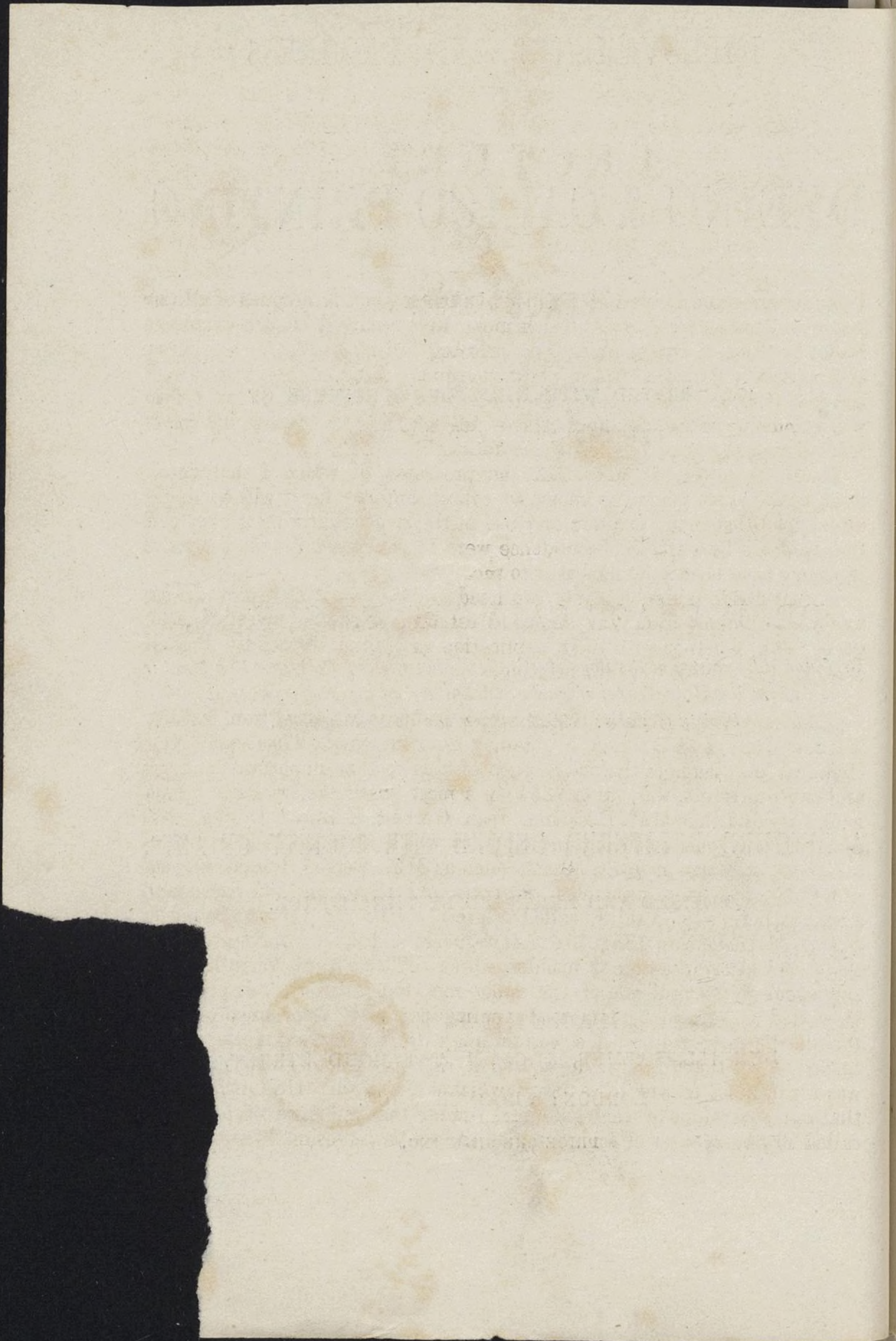
DUNNILL, PALMER, & CO., 1 & 3, BOND STREET.

LONDON: TRÜBNER & CO.

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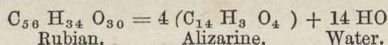
I CANNOT presume to give, in a paper like the present, an account of all the improvements and inventions which must have occurred in such extensive trades as those of dyeing and calico printing during a space of ten years, and especially during a decade of extraordinary progress like that which has just passed. The utmost, therefore, that I can do is, to lay before you an outline of the principal discoveries which have come to my knowledge during the period under consideration.

I wish, however, to state that the processes of which I shall speak to-night are those generally known to calico-printers; for it will be easily understood that many printers may use methods peculiarly their own, and that it would be a breach of confidence were I to publish any such processes that may have been communicated to me.

I shall divide the subject into two heads. First, treating of new dyeing materials obtained from well known dyestuffs, and then of dyestuffs altogether new, together with their application to dyeing. Secondly, I shall consider the subject of calico printing.

Madder.—This valuable dyestuff, which is chiefly imported from France, Turkey, Italy, and Holland, is obtained from the *Rubia Tinctorum*. Our chemical knowledge of the composition of this root, so important to dyers and calico printers, was, up to 1851, in a most unsatisfactory state. Thus, whilst we find that MM. Decaisne, Jean Gerber, Edmund Dollfus, &c., asserted only one colouring principle, to which they gave the names of *alizarine*, *colorine*, or *azale*, others, such as MM. Persoz, Ruuge, &c., admitted two colouring principles, *alizarine* and *purpurine*, and Kuhlmann added to these two, a third, called *xanthine*. But Dr. Edward Schunck, F.R.S., published, in 1851, his most valuable and extensive researches on the chemical composition of madder, which not only threw much light on the colour-giving principle of the rubia root, but also, as I will presently show, led to valuable commercial applications. He ascertained that, although the roots contained a certain quantity of colouring matter called *alizarine*, yet that the ultimate source of this only colour-giving principle, was a substance to which he gave the name of *rubian*. He further found that one equivalent of this substance under the influence of a ferment called *erythrozym*, or of acids, or alkalies, would, by losing 14 equivalents

of water, be converted into 4 equivalents of alizarine, as the following equation shows :—



This result satisfactorily explained the change of madder into garancine by the action of sulphuric acid on that root, from the fact that rubian was susceptible of conversion, under the same influences, not only into alizarine, but also into two valueless substances, called rubiretine and verantine. This led Mr. Simon Pincoffs, in conjunction with Dr. Schunck, in 1852, to the production of a most important dyeing material, called by them *commercial alizarine*. But to enable you to understand in what this product differs from garancine, and also its mode of preparation, it is necessary that I should state that the verantine and rubiretine are not colour-giving principles, and that they interfere with the beauty and brightness of the fine shades of purple given by alizarine, which, according to Dr. Schunck, is the only colour-giving principle contained in madder.*

Garancine, which, even before 1851, was extensively used for producing red, purple, and chocolate, upon calico, was obtained, as you are aware, either by mixing together at an ordinary temperature equal weights of madder and sulphuric acid, then adding water, when the garancine was produced, requiring only to be thoroughly washed so as to remove the acid;—or by mixing the roots with one third their weight of sulphuric acid previously diluted with water, and carrying the whole to the boil for one or two hours, washing the residue repeatedly, and using, in the last operation, some alkaline carbonate.

Specimens of Garancine Style.†



Although garancine thus prepared gave colours similar to madder, yet they were wanting in solidity. This effect, especially as regards purple, was overcome by Messrs. Pincoffs and Schunck by taking principally garancine prepared as above, but thoroughly depriving it of acid, and submitting it to the action of high-pressure steam, when the substance called verantine is decomposed or modified so as to stain the whites less and not to interfere with the purple-dyeing power of alizarine. The advantages possessed by this product, which is now so extensively employed in calico printing, that several millions of pieces have been dyed with it, are, as stated by Messrs. Pincoffs and Schunck, as follows :—It produces good

* Dr. Schunck also obtained as products of decomposition of rubian, rubianine and sugar. Those who are interested in these chemical researches will find them fully detailed in the Transactions of the Royal Society.

† We are indebted to Messrs. Wood and Wright for the above specimens.

lilacs economically and without soaping; great promptitude and regularity in the production; facility of producing combination of lilacs with catechu, and lilac and chocolate, which results cannot be obtained so satisfactorily with madder or garancine; production of lilac shades graduated *ad libitum* as to cost; lastly, economy of mordants. I shall again refer to this in speaking of calico printing.

The following are specimens of Alizarine Printing.



Whilst on this class of madder products, I may refer to an improvement effected by Mr. John Lightfoot, in the manufacture of garanceux, (which was discovered in 1843 by Mr. Schwartz), or spent madder, which has been treated with sulphuric acid, as above described, for the preparation of garancine. The method now generally followed is to collect the spent madder in bags as it runs from the dye becks, and then throwing it on to a heap, to be ultimately converted into garanceux, by acting upon it, as above described, with sulphuric acid. Mr. Lightfoot, however, recommends large vats to be provided, allowing to run into them the hot spent madder liquors of the dye becks, together with vitriol, leaving the whole to stand for 24 hours, running off the clear liquor and washing the solid garanceux thus produced, until all impurities and acid are removed. The advantages claimed are, first, saving of fuel, by economizing the heat of the waste liquors, and secondly, the production of one-fourth more colouring matter. Of late years the French calico printers have applied, for light styles of madder-pinks, extracts of madder, or garancine, which have generally been obtained by treating madders or garancines with alcohol or wood-spirit, and adding to them acetate of alumina and acetic acid; a similar process has recently been patented by Mr. F. A. Gatty. Another most interesting process has recently been published by Mr. Emile Kopp, for the production of alizarine from garancine. It consists in submitting dry garancine in a double cylinder to the action of superheated and saturated steam, when the alizarine is carried off by the steam, and the whole condensed in a refrigerator.

Flower of Madder.—This product, which is now extensively used by continental printers, and which was introduced to the trade by MM. Julian and Roquer towards the beginning of 1852, is prepared by allowing madder to ferment, and then washing it thoroughly, which removes from it, not only all soluble matters such as sugar, mucilaginous substances, acids, &c., which interfere with the fixation of the alizarine on the various mordants, but also (in accordance with Dr. Schunck's researches on the influence of the ferment erythrozym on rubian), increases the quantity of colour-giving principle or alizarine. It is found, by experience, that meny 100

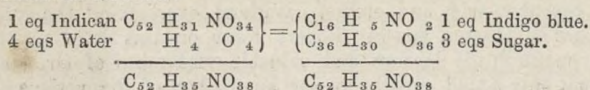
parts of flower of madder are equal to about 200 parts of ordinary ground roots, and that the shades are finer, the pinks and reds also having greater solidity. Mr. E. Mucklow has recently patented a process similar to the above, which consists in alternately macerating and pressing madder roots so as to expel from them various materials which, as above stated, interfere with the dyeing of the fabrics.

Mr. Emile Kopp has published a very interesting paper on the subject of madder, in which he proves that, if the madders of Alsace are treated with a weak solution of sulphurous acid, and to this solution, which has a fine golden colour, he adds three or four per cent. of hydrochloric acid, and heats the whole to a temperature of 150° , a red colouring matter is precipitated, which he states to be pure *purpurine*. If, after the separation of this precipitate, the liquor is again carried to the boil, a new colouring matter is formed, which he calls *green alizarine*, and finds to be composed of pure alizarine and a dark green resin, which he considers is produced by the decomposition of chlorogenine.

As a *resumé* of my observations on madder, I may state that the only two madder products which have received extensive application since 1851 are commercial alizarine and flower of madder.

Indigo.—I have the pleasure again to draw your attention to a series of researches by Dr. Edward Schunck, and to enable you to appreciate the value of his discoveries in connection with this important dyestuff, it is necessary that I should first state that chemists held two different opinions as to the condition in which the colouring matter existed in the indigo plants. Thus, Chevreul, Girardin, &c., considered that the indigo contained in the plant was in the form of white, or de-oxygenated blue indigo; whilst Giobert and others believed that it did not pre-exist in the vegetable, but was formed during the process of fermentation, which is usually employed for the extraction of the colour from the *Isatis tinctoria* and *Indigofera anil*. Serious doubts having arisen in the mind of Dr. Schunck, whether either of these theories correctly explained the state in which indigo existed in the indigo plant, he undertook a long series of researches, by which he was enabled to show, with a positive certainty, that the *Isatis tinctoria* contains a substance easily soluble in hot and cold water, alcohol, and ether, and which, by the action of strong mineral acid, yields indigo blue. Further, that the formation of the colouring matter from it can be effected without the intervention of oxygen or of alkalies, and that the latter, indeed, if allowed to act upon it before the application of acid, entirely prevents the formation of the colouring matter; viz., indigo blue. To ascertain whether the substance which he calls *indican*, pre-existed in the plant, Dr. Schunck operated as follows:—He digested in ether some perfectly dry leaves of the *Isatis tinctoria*, removed the ethereal solution, and having exposed it to spontaneous evaporation, it left a green syrupy residue, from which water extracted *indican*, for by the action of boiling sulphuric acid, it yielded an abundance of indigo blue. To obtain the *indican* in a high state of purity, he found it necessary to treat the leaves with alcohol and ether, and to submit the extract to various chemical operations, to get rid of all impurities, so as to obtain indican as a yellow transparent glutinous substance, of a slightly bitter and nauseous taste.

This substance presents the remarkable property (similar to that of rubian in madder) of being susceptible under the influence of a ferment in the plant, or of acids, of yielding indigo blue and sugar, as seen by the following chemical formula:—



To obtain this interesting decomposition with acids, it is simply necessary to heat the indican with strong sulphuric or hydrochloric acid; when the indigo blue precipitates while the sugar remains in solution. But indican is so liable to undergo modifications, that if the action of the acids be continued, besides the indigo blue an indigo purple is formed, called by Dr. Schunck *indirubine*. To fully appreciate the value of these researches it is necessary that I should lay before you an outline of the manufacture of indigo, as some of you may not be acquainted with it. Commercial indigo is obtained from plants belonging to the leguminous tribe, known under the general name of *indigofera*, that these plants are mowed and placed in large vats with water, and allowed to ferment for 8 or 10 hours, when the supernatant liquor first becomes green and then blue. It is then run off into other vats and well agitated, so as to bring it thoroughly under the action of the atmospheric oxygen, when the white soluble indigo becomes thoroughly oxydised into blue insoluble indigo. A little lime water is now added and the whole left to settle, the deposit collected on a cloth, drained, pressed, divided into square lumps, and dried in the sun, when it constitutes commercial indigo. Dr. Schunck's researches show, as above stated, that under the influence of a ferment the *indican* is converted into sugar and white indigo; and they also explain that if the manufacturer is not extremely careful he may experience great loss in the amount of indigo obtained, for Dr. Schunck has observed that *indican*, when dissolved in water, is liable to undergo rapid modifications, and that instead of yielding by the acids indigo blue and *indirubine*, it gives *indiretine*, *indihumine*, &c. You will, doubtless, be struck with the great similarity which exists between the colour giving principles of the madder and indigo plants, and with the light thrown upon this class of tinctorial matters by the laborious researches of Dr. Schunck. I cannot leave this interesting substance without stating that, although one or two attempts have been made to introduce new preparations of indigo, they have not, to my knowledge, yet received the sanction of the trade. Such are the preparations of the sulpho-indigotic acid of Mr. Haefly, the sulpho-purpurate of soda of Mr. Bolley, and the indigo of Mr. Johnson.

Orchil. It is hardly necessary for me to state that this dyestuff has been used for producing violets, mauves, reds, and other colours, for many years, and that the colouring matter was obtained by allowing lichens to remain in contact at natural temperature for several weeks with putrid urine and a little lime, and that of late years ammonia has been substituted for urine, with the addition of a little carbonate of soda, nitrate of soda, or alum. You are also doubtless aware that Robiquet was the first to obtain a colourless principle called *orcine*, and to show that under the

influence of oxygen and ammonia it became transformed into water and a red colour called *orcéine*, and that Dr. Schunck proved that a substance extracted by him under the name of *lecanoric acid*, from lichens, would, under the influence of heat and a solution of baryta, decompose itself into water, carbonic acid, and orcin. Without overlooking the interesting researches of Heeren and Sir Robert Kane on this subject, I must especially mention the labours and valuable researches of Dr. Stenhouse, which not only added greatly to our knowledge of the various chemical principles existing in lichens from which the orchil colouring matters are obtained, but also led him to discover a commercial method of extracting from the lichens the various organic substances capable of giving orchil colours when placed in favourable conditions. He also showed that the very small per-centage of colouring matters in proportion to the bulk of weed might be cheaply and commercially extracted in the locality where the lichens grow, thus saving the enormous expense of carrying a large bulk of useless matter from Africa and elsewhere to this country. If this valuable hint of Dr. Stenhouse's has not yet been acted upon as regards the saving of transport, his process for extracting the colour-giving principle has of late years been extensively adopted by manufacturers of orchil, enabling them to obtain cheaper and better colours from lichens. But still none of these advantages led manufacturers to the great desideratum of giving fastness to the beautiful purple shades obtained from orchils until 1856, when Mr. Marnas, of the firm of Guinon, Marnas, and Bonnet, of Lyons, found that by treating lichens, as suggested by Dr. Stenhouse, with milk of lime, filtering the lime liquor off and precipitating the colour-giving principle from it with hydrochloric acid, gathering these on a filter, and after having properly washed them, dissolving them in caustic ammonia, and keeping this ammoniacal liquor at a temperature of 153° to 160° for 20 to 25 days, when under the influence of that temperature, the colour-giving principles of the lichens fix ammonia and oxygen and are transformed into a new series of products, which Mr. Marnas separates from the coloured liquid by adding chloride of calcium, which causes a fine purple lake to be deposited, which, after being well washed and dried, is sold under the name of *French purple*. It is easy to understand that the chloride of calcium can be replaced by salts of alumina, tin, &c. What characterises this orchil colour from those previously known is, that it dyes animal fibres with greater facility than the common orchil, that it gives directly mauve colours, which can be modified by adding to them a little carmine of indigo, roseine, &c.; but the essential difference of these purples and mauves from ordinary orchil colours is—that while the latter are destroyed by acids and light, those of Mr. Marnas, on the contrary, withstand their action, thus accounting for the public favour given to Messrs. Guinon, Marnas, and Co.'s orchil colours. To dye silk or wool with French purple it is simply necessary to mix the lake with its weight of oxalic acid, boil with water and then filter, the oxalate of lime remaining on the filter while the colour passes in the filtrate. This liquor is then added to a slightly ammoniacal liquid contained in the dye-beck; all that is now necessary is to dip in the beck, silk, wool, cotton, mordanted with albumen, or cotton prepared for

*Silk dyed with
French purple.*



Turkey red, when any of these materials will become dyed with magnificent fast shades of purple or mauve. It is a curious coincidence that after many years of anxious search, two purples from widely different sources should have been first discovered in the same year (1856) in different countries. I allude to Mr. Perkin's purple from coal tar, to which I shall refer further on.

Catechu, or *Terra Japonica*, which is extracted from the wood of the acachia catechu, and which we import in large quantities from the East Indies, is daily becoming of increased importance, owing to the great variety of colours that can be obtained with it. It contains two very distinct substances, a tannin (studied by Dr. Stenhouse) which gives a green precipitate with salts of per-oxide of iron, and also a substance called *catechine*, which under the influence of alkalies and oxygen is rapidly transformed into two acids called japonic and rubinic acid. As in catechu, the tannin gives various shades of drab, the catechine giving, with proper metallic salts, salmon, red, and wood colours. Some calico printers have of late, under my advice, washed with cold water pulverised catechu, which dissolves freely the tannin, leaving the catechine insoluble in cold water, which, however, being soluble in hot water, becomes susceptible of application.

Aloes.—Owing to the interesting researches of Drs. Schunck and Stenhouse upon the resin obtained from the *aloe socotorina*, and imported from the East and West Indies as well as Africa, the various colouring matters obtained by them have, of late, been employed by the French dyers for producing pinks, violet, maroons, and other shades.

Lac Dye.—Messrs. Haworth and Brooke, of Manchester, have introduced into commerce a lac dye superior to that imported from India, which, as you are aware, is prepared from stick lac. Their improvement consists in treating stick lac with weak ammonia, and adding to this solution chloride of tin, when a fine red insoluble matter is formed which precipitates. This is collected, and is ready for use.

Chlorophyll.—For many years attempts were made to fix upon fabrics the green colouring matter of leaves, but unsuccessfully, until, in 1854, M. Hartmann and Cordillott, of Mulhouse, succeeded by the following simple process in obtaining on silk, wool, and cotton, fine green brilliant and solid colours. After having boiled a quantity of grass, so as to remove everything soluble in boiling water, it was heated with a hot caustic lye of specific gravity 1.03, this alkaline solution being then neutralized with hydrochloric acid, a fine green precipitate was thrown down. This precipitate was then dissolved in a solution of caustic lye, to which had been previously added some phosphate of soda and oxide of tin.* This mix-

* Any one who wishes for further information on the green colouring matter from plants, will find a most interesting paper by M. Fremy, published in the *Comptes Rendus* of the French Academy, for 1860, volume 50, in which that chemist shows that chlorophyll is composed of two colouring matters called phylloxanthine and phylloxyanine.

ture, properly thickened with gum, was printed and fixed by steaming. No doubt, by a slight modification in the *modus operandi*, this colour might be applied to dyeing.

Chinese Green, called *Lo-kao*.—In 1851 and 1852, public attention was drawn, by several English gentlemen, to samples of a green colouring matter, imported from China, and in 1853, Messrs. Guinon, of Lyons, imported such quantities of the material as to enable them to dye silks for the requirements of the trade. The silks so dyed by them, under the names of *Vert-Venus*, *Vert-Azof*, and *Vert-Lumiere*, were especially

Vert Lumiere.



admired, from the beautiful green shades they assumed in artificial light; and although the price of the dye fell from £21 per pound in 1853, to £4 in 1860, these beautiful shades of green (especially under artificial light) have almost disappeared from the market owing to the two following reasons:—first, their want of stability; and, secondly, because Messrs. Guinon, Marnas, and Bonnet, have found

the following means of producing, at less cost, shades of green which also maintain this character under the influence of artificial light, *i.e.* by first dyeing their silks in Prussian-blue, and then dyeing them in an acidulated bath of carboazotic, or picric acid. It is an interesting fact to observe that, while the greens produced with indigo and picric acid appear blue in artificial light, those produced as above with Prussian blue and picric acid appear green under the same conditions. I cannot leave this interesting subject without making two further remarks: First, *Lo-kao* is the only substance with which I am acquainted capable, with proper reagents, of producing the seven colours of the spectrum; secondly, that, thanks to the advanced state of chemical and botanical science, we have succeeded in producing, in Europe, the identical substance imported only a few years ago, as a great novelty, from China—and for which, but for those sciences, we should still probably have remained tributary to that empire. Thus Mr. Charvin, of Lyons, has been able to obtain *Lo-kao* from a weed indigenous to Europe, viz., *Rhamnus catharticus*, for which he has received, from the Chamber of Commerce of Lyons, a gold medal worth 6,000 francs.*

Murexide, or *Roman Purple*.—The colour to which I am now about to draw your attention furnishes another example of the assistance which the progress of chemical science has rendered to the art of calico printing. In 1776, the illustrious Swedish chemist, Scheele, discovered, in human urine, uric acid. In 1817, Brugnatelli found that nitric acid transformed uric acid into a substance, which he called *erythric acid*, but which was subsequently called by Wöhler and Liebig, *alloxan*. In 1818, Dr. Prout found that the latter substance gave, when in contact with ammonia, a beautiful purple red colour, which he called purpurate of ammonia—the product known by the name of *murexide* since the researches of Liebig and Wöhler, published about 1837. These discoveries remained dormant in the field of pure science until the year 1851, when Dr. Saac observed

* For full details on this subject, see Report presented to the Chamber of Commerce, at Lyons, by the Rev. M. Hélot, M. Persoz, &c.

that when alloxan came into contact with the hand it tinged it red. This led him to infer that alloxan might be employed to dye woollens red, and further experiments convinced him that if woollen cloth were prepared with a salt of tin, passed through a solution of alloxan, and then submitted to a gentle heat, a most beautiful and delicate pink colour resulted. In 1856, MM. Depouilly, Lauth, Meister, Petersen, and Albert Schlumberger, applied it as a dyeing material to silk and wool, and succeeded in obtaining red and purple colours, by mixing the murexide with corrosive sublimate, acetate of soda, and acetic acid. For printing, a mixture of murexide with nitric of lead and acetate of zinc, properly thickened, is applied on cotton fabrics, which are then allowed to dry for a day or two, when the colour is fixed by passing them through a mixture of corrosive sublimate, acetate of soda, and acetic acid. The Roman purple style of

Printed Murexide.



printing has been carried out extensively by Messrs. Edmund Potter and Co.; Boyd, Sons, and Hamel; James Black and Co. No doubt you will wonder whence such quantities of uric acid, or murexide, could be drawn to supply a demand like that which has arisen. This result has been achieved by the following process of extracting uric acid from Peruvian guano. Guano is treated repeatedly with hydrochloric acid, until all soluble matters are removed by heat and washing. The insoluble mass, which consists chiefly of sand and uric acid, is carefully treated with nitric acid of specific gravity of 1.40. When the action of the acid is completed, the mass is treated with warm water, and thrown on a filter. The filtrate, which has a yellowish colour, and contains alloxan, &c., is evaporated carefully to such a degree, that when left to cool it becomes a brownish red or violet solid, called by the inventor, *carmin de pourpre*, which is the substance chiefly used for printing, as above described. It is to the enterprising commercial spirit of Mr. Robert Rumney, chemical manufacturer, of Manchester, that is due the extensive production and application of murexide in this country.

Doubtless you are aware that alum, and cream of tartar, are used largely as mordants in the dyeing of silk, wool, and cotton, and that the latter substance has much risen in price, owing to the failure of the wine crops of late years; therefore, any process for economising the use of cream of tartar is a matter of importance. I am happy to state that Mr. Kuhlmann has, within the last few weeks, published in the *Mémoires* of the French Academy, a paper in which he furnishes a means of attaining that end. Having first confirmed a most important observation of Mr. Chevreul's, viz., that when cream of tartar is used as a mordant it is decomposed into tartaric acid, which adheres to the fibre, and into a neutral tartrate which remains in solution and is lost, and that if, on the contrary, instead of using the cream of tartar as a mordant, it is first decomposed into tartrate of baryta, and that this salt be used as a mordant, in connexion with a little hydrochloric acid, the two equivalents of the tartaric acid of the cream of tartar become available, and consequently a saving of one-half the quantity of cream of tartar formerly used is effected.

In the hope that it may prove interesting to the members of this Society, I will now give some details respecting a few new processes for dyeing silk, before proceeding to treat of coal tar colours.

Catechu Black.—The silks are first passed into a solution of salts of peroxide of iron, then into a hot soap solution containing an excess of soap, from whence they are passed into a slightly acid bath of prussiate of potash. The silks which have thus been dyed Prussian blue, are dipped into a solution of persalt of iron, having a specific gravity of 1.15, the object of which is to give an iron mordaunt to the silk. They are then thoroughly washed and passed into a bath of catechu for organzine at 203°, and for tram at 172°, the silks being worked in this bath until it is cold, so as to saturate thoroughly the iron mordaunt with the colouring principle of catechu, and thus produce a black. They are then wrung on the peg and exposed to the atmosphere for 24 hours, after which they are passed into a soap solution at 150°, washed thoroughly, and the organzine is then dipped in a bath of weak acetic acid, and the tram in one of weak hydrochloric acid; finally, the silks are passed through an emulsion of oil, well worked on the peg and allowed to dry. These last operations are intended to remove, by means of the fatty matters, the harshness which the silk would otherwise possess.

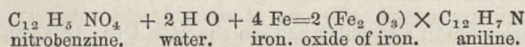
The following is a process for preparing dyed silks, so that when woven into fabrics these will be fit for taking the moire antique:—Two parts of pure olive oil are mixed with one of concentrated sulphuric acid, and agitated until sulphurous acid begins to be liberated. It is then well mixed with 15 parts of lukewarm water, and the whole further diluted with boiling water. The silks are then passed into this bath and then into a second similar bath, to which has been added a little free vitriol. After this, they are successively dipped in a hot bath containing a little citric acid, then into the previous No. 2, to which is added a little sulphate of alumina and a little black dye to restore to the silk any colour it may have lost during the former operations. The silks, after having been dried in the air, are ready for weaving. The object of these processes is to introduce into the silk fatty acids, the property of which is to communicate to the silk a great degree of softness, and adapt it to receive, by intense pressure, the intended moire.

I will now describe a process for dyeing silks white. The silks, after having been boiled, are first passed into a slightly ammoniacal bath, and from thence into another of water, in which has been dissolved a little French purple, and lastly, into another bath containing lukewarm water, to which is added, in successive portions, some carmine of indigo, and the silks are then dried. Many of you will doubtless remember that in my papers read here in 1851, I explained that, when the three primitive colours of the spectrum are mixed in due proportions, they produce white if reflected, and black if absorbed. The French purple gives the red; the carmine of indigo blue; and the silk itself the required yellow.

Several improvements have also taken place in the production of maroons, greens, and Prussian blues, but time will not allow of my laying the details before you.

Colours derived from Coal Tar.—These colours are as interesting for

their beauty and brilliancy as for the source whence they are derived, and present a remarkable instance of the valuable services which abstract science so frequently renders to the material interests of society. How little did even chemists dream that a substance first perceived by Unverdorben in the year 1826, then named *aniline* by Fritsche, and discovered in coal tar about 1841, by Dr. A. W. Hofmann, would lead to the production of such magnificent colours as aniline purple, magenta, &c. There can be no doubt that it is to the interesting and learned researches of Dr. Hofmann on aniline, that we owe the possession of these splendid colours, and further, it was one of his pupils, Mr. W. A. Perkin, who produced for the first time, on a commercial scale, aniline, and then the splendid purple colour which it is susceptible of yielding. Before describing to you the process patented by Mr. Perkin in 1856 to produce his purple, allow me to lay before you an outline of the present plan followed for obtaining aniline. A carburetted hydrogen, which I mentioned to you in one of my previous papers, called "Benzine" ($C_{12}H_6$), and obtained by the careful distillation of purified coal naphtha at a temperature of about 186° , is treated with strong nitric acid, when a violent action ensues, which gives rise to nitrobenzine or $C_{12}H_5NO_4$. To convert this compound into aniline, one hundred parts of nitrobenzine are mixed with an equal quantity of acetic acid, and 200 parts iron filings, heat is produced, and the following chemical action ensues:—



The whole is then introduced into a retort, and the raw product which passes from it is mixed with a little alkali or lime, and again distilled, when aniline is obtained. This important substance is, as you perceive, a colourless fluid, which boils at 359° , has a decided alkaline reaction, and sp. gr. of 1.028. The following is the process described by Mr. Perkin for preparing his purple. Solutions containing equivalent proportions of sulphate of aniline and bichromate of potash are mixed and allowed to stand till the reaction is complete. The resulting black precipitate is then thrown on to a filter and washed with water until free from sulphate of potash; it is then dried. This dried product is afterwards digested several times with coal tar naphtha until all resinous matter is separated, and the naphtha is no longer coloured brown. After this it is repeatedly boiled with alcohol to extract the colouring matter. This alcoholic solution when distilled leaves the colouring matter at the bottom of the retort as a beautiful bronze coloured substance, which may be considered as Mr. Perkin's commercial aniline purple. This colour, which can also be produced by oxidising aniline by other metallic salts, is slightly soluble in water, freely soluble in alcohol, and presents the remarkable property of not being affected by light, alkalies, or acids. To dye wool or silk with it, it is simply necessary to add to a hot water bath, slightly acidulated with tartaric acid, some of the alcoholic solution of aniline purple, and to work the silk in the said bath, wringing and washing it; the purple shade thus produced can be modified with roseine, Prussian blue, or sulphate of indigo. To dye cotton so as to resist the action of soap and light, the

*Silk dyed with Purple
Aniline.*



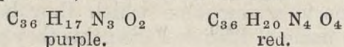
process is modified so as to form on the cotton fibre an insoluble compound of colouring matter with tannin and a metallic base. To effect this the cotton is passed for an hour or two in a bath containing a tanning substance, and then into a weak solution of stannate of soda, wrung out, passed into an acid liquor, rinsed in water, and then, like silk, dipped into an acidulated bath of purple aniline. Also cotton prepared with a basic salt of lead, or as for Turkey red, will take up aniline purple. On the 12th January 1861, another interesting process to obtain aniline purple was patented by Mr. Adam Girard. Pure red aniline (known in this country as magenta), is mixed with an equal weight of aniline, and the mixture heated for several hours to 320° , when the mass is changed to a fine purple colour, requiring only to be mixed with water and hydrochloric acid, to remove any aniline or red dye in excess, leaving the purple insoluble, but on being well washed with water, this becomes soluble in alcohol, acetic acid, wood naphtha, and boiling water slightly acidulated with acetic acid.

Whilst on this mode of producing purple aniline, I may say that blue dye may also be obtained with the above insoluble purple residue by boiling it several times with hydrochloric acid diluted, say ten parts of commercial acid to 100 parts of water, when the purple is converted into a blue dye.

Mr. Charles Lauth also published, on the 24th Dec., 1860, an ingenious method of obtaining purple aniline, which I shall describe when treating of blue colours obtained from aniline.

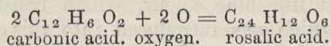
Red dyes obtained from aniline, called fuchsine, azaléine, roseine, &c.—The production of the fine colour, which bears the popular name of Magenta, was first observed by Mr. Natanson, in 1856, and more especially by Dr. Hofmann when preparing cyantriphenyl-diamine, by the action of bichloride of carbon on aniline. But it was Mr. Verguin who first brought it forward to the trade as a dyeing agent, and his mode of preparation which was patented in April, 1859, by Messrs. Renard and Franc, of Lyons, is the following:—Into a glazed iron pan are introduced 100 parts of aniline and 60 parts of anhydrous bichloride of tin, and the whole is heated for 15 or twenty minutes, at a temperature of about 392° . The dark red liquor thus produced is left to cool, when it becomes thick and glutinous; it is then mixed with boiling water and filtered; to the filtrate is added chloride of sodium, which determines the precipitation of fuchsine, as it is insoluble in saline solutions. Magenta was afterwards prepared by Mr. C. Greville Williams, with permanganate of potash, and by Dr. D. Price, with binoxide of lead; nitric acid, and nitrate of mercury were also successfully employed. These different methods of preparing magenta were followed by several other patents, purporting to obtain the same results, and amongst them I may cite that taken on the 10th December, 1859, by Mr. Rudolph Heilmann, in which the employment of arsenic acid is mentioned, and one also for the employment of the same agent on the 18th of January, 1860, by Dr. H. Medlock. As it is probable that this agent is the best suited for producing magenta, commercially, I will

give a sketch of the process. Dr. Medlock heats two parts of aniline with one of arsenic acid to about 250° , and when the red colour is produced it is mixed with boiling water and allowed to cool. The red colour is thrown down by saline matter, washed, and dissolved in methylated alcohol, or the mass is digested in hydrochloric acid diluted with water, and the clear fluid solution is saturated with an excess of soda which precipitates the colour, while the arsenic acid is held in solution by the alkali. Magenta is a rather powerful organic base which is sparingly soluble in water, but its solubility is increased by the presence of an acid. It leaves a brittle mass, having a beautiful golden green metallic reflection when its alcoholic solution is left to spontaneous evaporation, and this is not peculiar to magenta, as the whole of the coal tar colours, when in a high state of purity, present the same appearance. Purple aniline differs from the red, not only in its composition, which is as follows—



but also because the fuschine dissolves in ammonia and in sulphuric acid with a yellow colour, and is discoloured by sulphurous acid, whilst the purple is unaffected by those reagents. Silk or wool is dyed with fuschine by simply adding some of the colour to a slightly acidulated bath. The dyeing power of this material is so great that 10 grains will dye 2 square yards of silk.

Rosalic Acid.—This beautiful redecouring matter, also derived from coal tar, and first described by Runge, in 1834, has been of late years studied by Dr. Angus Smith, of Manchester, and Mr. Jourdain one of my assistants. Dr. Angus Smith in an interesting paper published in the Memoirs of the Manchester Literary and Philosophical Society for the year 1860, gives some interesting details respecting its properties, and shows that its production is due to the direct oxydation of another coal tar product called carbolic acid, for

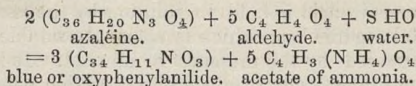


Mr. Jourdain in a paper recently published perfectly confirms the results obtained by Dr. Angus Smith, but gives more active means of oxydising the carbolic acid by passing vapour of carbolic acid, at a temperature of 302° over a mixture of binoxide of mercury and soda, when rosolate of soda is readily formed. It is then only necessary to neutralize the soda to liberate the rosalic acid. Of late years many attempts have been made to fix this colour, but up to the present time I believe all attempts have failed, with the exception of rosolate of magnesia, which was employed for some time in calico printing.

Blue colouring matters from Coal Tar—I have already drawn your attention to the blue colouring matter patented by Mr. Girard, and carried out practically by Messrs. Renard and Franc, of Lyons. Mr. Lauth also has observed that if an alcoholic solution of red aniline, and especially azaléine, is heated with a reducing agent, such as protochloride of tin, or still better with aldehyde or hydruret of benzoile, a blue colour is produced

even at ordinary temperatures. This blue colour is soluble in water, alcohol, and acetic acid, but does not resist the action of mineral acids, alkalies, or light.

Mr. Willm has recently published an interesting paper on this aniline blue, which not only shows how aldehyde acts, but exhibits the composition of the blue itself.



Therefore the triamine azaléine has been transformed into a monamine blue, by a new chemical reaction, for aldehyde not only acts as a reducing agent, but converts a part of the nitrogen into ammonia.

Bleu de Paris.—Recently, Messrs. Persoz, de Luynes and Salvétat called public attention to a new blue which they had produced, and to which they gave the name of Bleu de Paris; this they prepared by heating for thirty hours, in a sealed tube, at a temperature of 356° , one part of anhydrous bichloride of mercury with two parts of aniline. The blue thus produced can resist the action of weak acids and alkalies, but assumes a red hue when acted on by these agents in a concentrated state. Sulphurous acid has no action upon it, and it dyes animal fibres with facility.

This colour is a good example of an aniline blue, as it can be obtained in perfectly defined crystals, having a light transparent hue, which are soluble in water, alcohol, wood naphtha, and acetic acid, but insoluble in ether and bisulphate of carbon.

Bleu de Mulhouse.—MM. Gros-Renaud and Schaeffer have lately published an interesting process for obtaining from the red aniline, called azaléine, a purple and a blue. It consists in dissolving in a litre of boiling water, 50 grammes of white gum lac in powder, and 18 grammes of carbonate of soda, to which is added 50 grammes of an alcoholic solution of azaléine. After an hour's ebullition, the red colour is transformed into the Bleu de Mulhouse.

Azuline.—This beautiful blue colour, which resists the action of the strongest acids, and which was introduced into this country at the latter end of 1860, by Messrs. Guinon, Marnas, and Bonnet, of Lyons, is prepared by them from phenic acid, and, when pure, presents itself under the form of copper-bronze coloured crystals, soluble in alcohol, to which they communicate a magnificent blue colour, slightly tinged with red. The following is the process for dyeing silk and wool:—To an acidulated lukewarm bath of water an alcoholic solution of azuline is added, and the silk

Specimen of Azuline. or wool worked in it until it is of the required shade. It is then transferred to another bath of boiling water, strongly acidulated with sulphuric acid, when the purple colour is dissolved, leaving a most brilliant and permanent blue upon the material. The dyed silk or wool is washed repeatedly, passed through a bath containing a little tartaric acid, and dried.

Chinoline Blue.—Mr. C. Greville Williams introduced in the spring of last year a fine blue colour, which he obtained by boiling together a substance derived from quinine or cinchonine called chinoline, with iodide of

amyl. The resulting product is boiled with water and then with potash for a quarter of an hour, filtered to separate the resinous matter, when a gorgeous blue is obtained, with scarcely any shade of red. This colour is so fugitive that its use has ceased.

Green Colours from Aniline.—Although it has been known to chemists that aniline would yield a green colour under certain oxidising agents, up to the present time all efforts to dye silk or wool commercially with it have failed, but to avoid having to refer to this green colour again I may mention that Messrs. Samuel Cliff, Charles Lowe, and myself, patented, on the 11th of June, 1860, a most easy and practical method of producing it under the name of *Emeraldine*, on cotton fabrics, specimens of which I have the honour to show you. The process consists in printing an acid chloride of aniline on a cotton fabric prepared with chlorate of potash, and in a few hours a beautiful bright green gradually appears, which only requires to be washed. If the green fabric is passed through a solution of bichromate of potash, this colour is transformed into a dark indigo blue, called by us *azurine*.

Naphthaline Colours.—The beautiful solid hydro-carbon naphthaline, which has yielded such a long category of substances to the chemists, has up to the present time yielded nothing of practical importance to the dyer, with the exception of a case which I shall mention presently. From it the following coloured derivatives have been obtained, namely, chloroxynaphthalic acid, perchloroxynaphthalic acid, carminaphtha, ninaphthalamine nitronaphthalin, naphthamein, and a body of a purple colour. It is to Mr. Perkin that we owe the knowledge of several of these substances and their colour-giving properties.* In my laboratory a fine purple colour has been obtained from naphthaline, which dyes with facility silk and wool.

A few months ago the scientific world were startled by the announcement, from a French chemist named Z. Roussin, that he believed he had discovered the means of making from naphthaline the important colour-giving principle which I have already mentioned to you when speaking of madder, called alizarine; and what strengthened his belief was, that he thought he had succeeded in removing two equivalents of oxygen from binitronaphthaline, and transforming the nitrogen thereof into ammonia, leaving, as a residue, alizarine, as seen by his formula:—

Binitronaphthaline	C_{12}, H_6, N_2, O_8
Minus oxygen	$- O_2$
Plus hydrogen	$+ H_6, H_2$
EQUALS				
Alizarine	C_{12}, H_6, O_6
Plus ammonia	N_2, H_6
Plus water	$2HO$

The simple process which he devised to obtain a crystalline substance which gave a red colour with an alumina mordant, consists in dissolving slowly binitronaphthaline in concentrated sulphuric acid, and raising the temperature gradually to 392°, when he adds granulated zinc in succes-

* Those who may wish for further information on the subject of coal tar colours, should consult the number for October, 1861, of the quarterly journal of the Chemical Society, which contains a valuable paper by Mr. W. A. Perkin.

sive small portions. After a short time sulphurous acid is given off, and the conversion of binitronaphthaline into a red colouring matter is effected. All that is now required is to dilute the liquor with eight or ten times its volume of water, and carrying it to the boil, filter, and allow the whole to cool, when Mr. Roussin's so-called alizarine deposits under the form of fine red or orange-coloured crystals. Although this product possesses some properties similar to those of alizarine, it differs from it in many of its chemical reactions, and also because it does not furnish the purple and chocolate colours given by alizarine with iron, and iron and alumina mordants. Still these results, arrived at by Mr. Roussin, are so remarkable that it is to be hoped he will persevere in his endeavours to solve this interesting problem.

I cannot conclude this part of my paper without drawing the attention of those interested in the subject of colours, to a series of valuable papers, which have recently been published in the memoirs of the Institute of France, by my eminent and learned master, M. Chevreul, on the comparative affinity of various colouring matters for different fibres, on the influence of various mordants, on divers colouring matters, and, lastly, on the influence of the solar light on such dyed fabrics.

CALICO PRINTING.

The art of calico printing depends upon so many branches, of mechanical as well as of chemical science, that it is impossible for me to give detailed information of all the improvements which every department of this manufacture has undergone, during the period embraced by this lecture, but I shall draw your attention to a few of the prominent points that have come under my notice.

Engraving of Rollers.—This branch of calico printing has made great progress. Not only have the engravings acquired sharper outlines and finer details, but the methods of engraving have greatly multiplied. I may cite as instances the application of the principle of the pentagraph, by Messrs. Smith, so as to trace patterns on the surface of rollers. Also, calico printers have extensively availed themselves of Mr. Lockett's improvements for producing the groundwork of prints, or as they are termed "covers," by applying "eccentric engraving," or etching, which produces with facility most complicated patterns on a varnished roller, by means of a diamond point guided by machinery. Another improvement, highly interesting in a scientific point of view, is the application of galvanism to the diamond tracer. By combining the galvanic action with an eccentric motion, most beautiful and delicate engravings may be produced. This is done by tracing the pattern with varnish on a zinc cylinder, which is so placed in the engraving machine that as a needle passes over its surface and comes into contact with the zinc, the galvanic current is established, and by simple machinery causes the diamond to trace the corresponding pattern on the copper roller. The communication is so rapid and precise that a great saving of time is effected. But if mechanical art has greatly

assisted the engraver, chemistry has rendered him equally important services, by enabling him to abandon costly and cumbrous modes of impressing by force the designs on the cylinder, substituting for them a great number of etching processes. By some of these processes, as by every other addition to the resources of the engraver, an entirely new and beautiful class of engraving is produced, unattainable by any other known means. For instance, owing to various improvements, rollers of 43 inches in circumference and 44 inches long have been introduced, enabling the calico printer to produce cheaply large furniture patterns.

En passant, I wish to call your attention to an application which has been made of a process greatly admired by many of you at the Exhibition of 1851, invented by Mr. John Mercer, the eminent calico printer, by which the beauty of dyed and printed goods was increased by passing the cotton fabrics through a strong solution of caustic lye, and afterwards through a weak solution of sulphuric acid, and then thoroughly washing. If this process has not been generally adopted, it is no doubt owing to the contraction which the cotton fibres experience under the above chemical influences, but the increased strength which the fibre thus acquires has been turned to good account, by enabling the printer to use it as a substitute for what is technically termed the "blanket" that is an endless cloth which passes over the engraved rollers with the goods to be printed. This material is found by its strength to resist better than most others the heavy strain which the blankets have to undergo during printing.

Singeing.—I shall here also allude to two improvements effected by Mr. John Thom, of Manchester. The first, applicable to all kinds of cotton or woollen fabrics, destined for printing or dyeing, consists in an improvement in the singeing or removing the nap from fabrics. The usual mode is to pass the fabrics either through a gas flame, or over a semi-circular heated iron plate. In the latter case, however, a large amount of fuel was wasted in maintaining the heat of the plate, owing to the free radiation of heat into the atmosphere, and to its absorption in the currents of cold air in contact with the plate. Mr. Thom's invention remedies these defects, by enclosing the plate under a brick arch, so that no air can enter the chamber except that which passes with the piece, and that limited quantity is, by a proper arrangement of flues, conducted into the furnace which heats the plate.

Messrs. Joshua Schofield and Sons have introduced a new machine, for singeing with gas, patented by Mr. James Cooke, which ingenious mode of singeing differs from the old method, in that instead of the gas flame being drawn through the fabric it is made to flow upon the surface, thereby removing the nap without destroying the loose fibres in the interstices. In consequence of the great heat of the flame, which is a mixture of coal gas and oxygen, the goods can be passed over with such rapidity as to remove the nap without injuring the fabric, a great advantage for fustians and heavy goods. To give an idea of the rapidity and consequent economy of this process, it is stated, that at Messrs. Edmund Potter and Co.'s works, more than 4000 pieces of calico have been singed in a day with this machine. Lastly, this machine, which consumes only 1000 feet of gas for 1000 pieces, has the same advantage as that of Mr. Thom, viz. : that it does not allow the fumes from singeing to create any offensive odour.

Sulphuring.—The second improvement of Mr. Thom was devised some years ago, but it is only recently that it has come into general use amongst printers. It is especially applicable to mixed fabrics, such as *mousselines de-laine*, which require, after they have been singed and before they are printed, to be bleached. This was formerly effected by hanging, for several hours, the moist pieces in chambers filled with sulphurous fumes, and is now performed by Mr. Thom's process in a few minutes, by passing them over a number of rollers confined in a chamber filled with the same vapours.

Thickening Substances.—It will be readily understood that it is necessary that the mordants or colours to be printed, should be of sufficient consistency to remain on those parts of the fabrics when they are left by the rollers, so as to produce sharply-defined patterns, and as a great variety of chemical products are employed a great variety of thickeners becomes also necessary. Thus flour, starch, farina, various natural gums, albumen, lactarine, gluten, and several preparations of flour and starch called calcined farina, and patent gums are used. For details of the improvements effected in patent gums I must refer you to the lecture which I had the honour to deliver, on the 21st December, 1852, before this Society.

Madder Styles.—Although there has been no marked change in this important branch of calico printing, still there are one or two departments in which considerable improvements have been effected, to which I desire to draw your attention, and to enable you better to understand the nature of these improvements, I shall describe them in the order in which they come into play in the production of this class of goods. The first is the improvements in patterns, arising out of the before-mentioned advances in the art of engraving. Secondly, a saving in the quantity of mordant used; for the fact which I have already stated with reference to commercial alizarine, viz., that weaker mordants are required, has been proved by Mr. Pincoffs to hold good with all the other preparations of madder, the strength of the mordant required to obtain the same intensity of shade being less, in proportion as the colouring matter is purer. It is also advisable that I should here state that the mordants generally used for madder styles, are the pyrolignites, or acetates of iron and alumina, which under the influence of "ageing," to be described presently, are so decomposed or modified as to leave on the cloth, either an insoluble oxide or subsalt, which becomes the intermediate agent for fixing on the fabric the colouring matter called alizarine, iron giving from a dark purple to a light lilac, alumina from a dark red to a pink, and a mixture of these two mordants a variety of chocolate tints. Thirdly, the most important improvement which has taken place in this branch of printing, viz., a great saving of time and labour in the fixing of mordants by ageing, was first practically carried out by Mr. Walter Crum, the eminent scientific calico printer. Dr. Schunck says that, "On the proper ageing of printed goods depends, in a great measure, the success of many styles; should a room be too hot or too dry, imperfect fixation of the colour ensues, and meagre and uneven tints are obtained in the subsequent operations. To give a further idea of the importance of this step in calico-printing, I may state that 'ageing-rooms' as they are called, are in several

print works of enormous dimensions, and are generally separate buildings. Those of Messrs. Edmund Potter and Co., and Messrs. Thomas Hoyle and Co., may be particularised as forming quite a feature in their works." The process of "ageing" in calico printing is that by which a mordant, after being applied to a cotton fabric, is placed in circumstances favourable to its being completely incorporated with, and fixed in the fibre. It has generally been found desirable that calico printed with a mordant, should, before dyeing, be exposed to the atmosphere for some time in the ageing-room in single folds, which, generally speaking, requires several days, the object being, as before stated, to liberate the acetic acid from the acetates of iron or sulpho-acetate of alumina, and to oxydise the oxide of iron. It was for many years believed that oxygen was the only necessary agent, and although some printers had observed that moisture facilitated the process, this fact was not generally known until Mr. John Thom, of Manchester, claimed the introduction of moisture as an important agent in the phenomena of ageing, in a patent which he took out in 1849. The first printer, however, who, as far as I am aware, practically applied this principle, was Mr. Walter Crum, F.R.S. But I cannot better show you the great saving effected by the judicious employment of steam in this process, than by giving you, in Mr. Crum's own words, the particulars of the plan adopted at Thornliebank print-works:—

"A building is employed 48 feet long inside and 40 feet high, with a mid-wall from bottom to top running lengthwise, so as to form two apartments each 11 feet wide. The manner in which they are fitted up will be understood by reference to the drawing.

"In one of these apartments the goods first receive the moisture they require. Besides the ground floor, it has two open sparrowed floors 26 feet apart, upon each of which is fixed a row of tin rollers, all long enough to contain two pieces of cloth at their breadth. The rollers being threaded, are set in motion by a small steam-engine, and the goods to be aged, which are at first placed in the ground floor, are drawn into the chamber above, where they are made to pass over and under each roller, issuing at last at the opposite end (on the right-hand side of the drawing) where they are folded into bundles on one (at a time) of the three stages which are placed there. These stages are partially separated from the rest of the chamber by woollen cloths.

"While the goods are traversing these rollers, they are exposed to heat and moisture, furnished to them by steam, which is made to issue gently from three rows of trumpet-mouth openings. The temperature is raised from 80 to 100 degrees, or more of Fahrenheit—a wet-bulb thermometer indicating at the same time 76 to 96 degrees, or always 4 degrees less than the dry-bulb thermometer. In this arrangement 50 pieces of 25 yards are exposed at one time, and as each piece is a quarter of an hour under the influence of the steam, 200 pieces pass through in an hour. Although workpeople need scarcely ever enter the warmest part of this chamber, a ventilator in the roof is opened when there is any considerable evolution of acetic acid.

"The mordant, as already explained, does not become fully "aged" by this process alone, although as much so as if it had hung a whole day

in cold air. It has received, however, the requisite quantity of moisture (about 7 per cent. of the weight of the printed piece), and is thereby enabled, if an iron mordant, to take oxygen from the air, and to become changed (with time) into the sesquiacetate and sesquihydrate of iron. In order to be sufficiently aged, it must be left one or two, or even three days in an atmosphere still warm and moist.

"It had fortunately been ascertained long before, at Thornliebank, that exposure in single folds after moistening was not necessary. Mr. Graham's experiments on the diffusion of gases through small apertures had served to suggest that for the absorption of the small quantity of oxygen required, the goods might as well be wrapped up and laid in heaps. Accordingly, in the operation in question, the moistened goods are carried in bundles into the building on the opposite side of the mid-wall already mentioned, and deposited there upon the sparred floors which are placed there at heights corresponding with the stages in the first apartment on which the goods are folded down. Upon these floors seven or eight thousand pieces may be laid at a time, and as each piece is 25 yards long, 100 miles is therefore the quantity that can be stored at once. It is necessary, of course, that an elevated temperature, and a corresponding degree of moisture, be preserved in the storing apartments day and night, and 80° Fahr. is sufficient with the wet bulb at 76°. To effect that object a large iron pipe is placed along the ground-floor underneath, and moderately heated by steam, while a row of small jets in the same position are made to project steam directly into the air of the apartment. The whole building is defended from external cold, and consequently from condensation of steam, by a warmed entrance room, and by double windows and double roof. Small steam pipes are also placed at other points where they seem to be required; and the apartment with rollers is specially heated, when not in use, by a couple of steam pipes, which are placed under the ceiling of the ground floor.

"The process of ageing, as thus detailed, was in operation at Thornliebank, in the autumn of 1856. About a year afterwards it began to be adopted by other printers, and now it is already in use at, at least, sixteen different printing establishments in Scotland and in Lancashire."

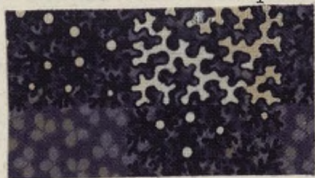
Fourthly, *Dung Substitutes*.—During the last few years the various dung substitutes, such as the double phosphate of soda and lime, the arsenites and arseniates of soda, and the silicates of soda have completely taken the place of cow dung in the process of dunging, that is to say, a process which consists in passing the mordanted and aged cloth into weak and hot solutions of the above-named substances, with a view of fixing thoroughly the mordant in the cloth, and removing any excess that may have been used, without allowing it to fix itself on the white, or unmordanted parts. By the introduction of these dung substitutes, and improved dunging vats, a great saving of time, labour, and expense has been effected. Thousands of pieces are now done in the same vat, where formerly as many hundreds only could be so heated.

Fifthly, *Washing Machines*.—As madder goods have to be thoroughly washed, not only after this operation, but also after dyeing, several improved machines have been introduced in the trade. I shall only here

mention those of Messrs. Mather and Platt, Mr. Furnival, Mr. D. Crawford, the last of which is much used for steam work and loose colours, and especially that of Mr. Thomas Whittaker, which I have heard highly praised by madder and garancine printers, and a model of which I have the pleasure to lay before you, through the kindness of Messrs. Christopher Whittaker and Co. To give you an idea of the vast capabilities of some of those machines, I will cite the following fact mentioned by Messrs. Whittaker.—"Our machine will wash 6,000 yards for all kinds of dyeing purposes, and 12,000 yards for all bleaching purposes, per hour (which only requires the attention of a person of 12 or 14 years of age)."

Sixthly. After the madder goods have undergone the above improved processes they are ready for the dyebeck, where the mordants assume the colours for which they are adapted. Here, also, a slight improvement has been effected, the advantage of which is a saving of time; as it now requires for saturating the mordants with alizarine only $1\frac{1}{2}$ hours for garancine and 2 hours for madder. After leaving the dyebecks the pieces are thoroughly washed in the improved washing machines, but as the white parts (or those not mordanted) are still soiled and the colours dim, it is necessary to pass the pieces for half an hour into a rather strong soap solution heated to 180° , when the loose dye is not only removed from the white parts, but also from the parts on which colour has been fixed. To finally brighten the colours and completely clean the white portions, the pieces are passed into a weak solution of what is called "chimic" or an alkaline hypo-chlorite of soda, with a little sulphate of zinc, until the desired effect is obtained, but latterly this process has been improved by passing the goods rapidly into chimic and then through a steam-chest. As the pieces have not yet, however, a commercial appearance, they further undergo what is called finishing, that is, the pieces are passed through a solution of sour flour (flour which has been fermented for several weeks), starch, farina, &c., and then between rollers, dried, and lastly through calenders, the object of which is to fill up the interstices of the fabrics and to give them a glossy appearance.

Specimens of Madder styles.



Much improvement has also taken place in this department of printing by the introduction of new machinery, especially in the methods of adapting the finish to the various markets of the world. I wish to take this opportunity of impressing upon printers the importance of dispensing, as much as possible, with the use of sour flour, and confining themselves to that of starch or farina, with the addition of about 1 ounce of sulphate of zinc per piece, for the purpose of diminishing the risk of mildew and other stains, to which a low class of printed goods are liable, during their transit in tropical climates, and especially those dyed with common garancine, bark, sumach, and peachwood.

In concluding my remarks upon madder, I wish to draw your attention to these beautiful examples of madder styles, for which I am indebted to Messrs. Symonds, Cunliffe, and Co., and of garancine styles to Messrs. Wood and Wright.

Indigo.—Most of the styles obtained with this valuable dye-stuff are due to the mixture of printing and dyeing, and only a few improvements have been effected herein, to my knowledge, during the last ten years.

First, the usual method of dyeing cotton, plain or self blue, is to fill with water large stone vats, and dissolving in them two parts of sulphate of protoxide of iron, adding one part of finely ground indigo, and then three parts of hydrate of lime. After having well stirred the whole for several hours, pieces of calico which have been hooked on a frame, and dipped in lime water, are then plunged for 15 minutes into the vat, when the blue indigo which has been converted into white indigo by the protoxide of iron, and rendered soluble by the excess of lime, fixes itself on the fibre, and, on the exposure of the latter to the atmosphere, re-absorbs oxygen and becomes blue. When white patterns are required, the pieces are printed before dyeing with what is called a "reserve," that is, a composition which prevents the colour from fixing itself on the fibre; the chief ingredient for that purpose is sulphate of copper, which acts by prematurely oxydising the indigo, and thus preventing its fixation. In

*Specimen of reserve
indigo blue.*



both these cases the pieces are passed through a weak sulphuric acid bath to perfectly fix the indigo, and formerly the copper thereby liberated from the fabrics was completely lost. Mr. Joseph Leese has recently devised a method of saving this valuable metal. To effect this, the diluted solution of sulphate of copper is made to filter through vessels containing wrought-iron turnings, the acid thus dissolving the iron, which may be used as sulphate of protoxide of

iron for future operations whilst the copper deposited on the excess of iron employed may be used, if thought fit, to manufacture again sulphate of copper. To give an idea of this process, I may state that the sulphate of copper used by one firm amounted to £3,000 a year.

Secondly. A few years ago I was able also to effect an economy in this branch of calico printing, which consisted in extracting from the cold indigo vats which were considered by the printer to be exhausted, a considerable per-centage of the indigo originally employed. Having observed that a green insoluble flocculent matter, which remained in the vats, and which was considered by chemists and printers to be simply oxide of iron, was in reality a compound of indigo and iron, I devised the following simple means of extracting the indigo therefrom:—The green pulp alluded to was conveyed from the several exhausted indigo vats into a general receptacle, and there mixed, first with a small quantity of hydrochloric acid, so as to remove the excess of lime, allowing the green pulp to settle, and running off the liquor. The so purified green pulp was then treated with strong hydrochloric acid, when chloride of iron was produced, and the indigo liberated, which required only to be washed to become again fit for use.

Thirdly. Although the printing of indigo offers great difficulty, still several printers have recourse to it from time to time, with greater or less success. The usual method of printing indigo consisted in mixing finely-powdered indigo with orpiment, or protochloride of tin, with a caustic alkali, and this process was further facilitated by printing the pieces in an atmosphere of coal gas, as devised by Mr. Bennett Woodcroft, the present learned officer of the Great Seal Patent Office, and carried out by Messrs. T. Hoyle and Sons, of Manchester. But of late years Mr. Joseph Leese, of Messrs. Kershaw, Leese, and Co., has succeeded in applying the following method, first devised by Mr. Fritzsche. The indigo is finely ground, and reduced to an impalpable powder, and then mixed with glucose, lime, and caustic soda, in such proportions as are needed to produce the shade of colour required. These materials are all mixed cold, and after the cloth is printed with the mixture it is passed through a steam

Printed Indigo.



chest, in which it is exposed for the space of from 30 to 60 seconds. In this short period the indigo is completely reduced and rendered soluble, when it enters into the fibre, and on emerging from the steam chest it becomes oxydised and fixed by exposure to the atmosphere, or the pieces may be immersed in a solution of an oxydising agent, such as dilute sulphate of copper, after which they only require to be washed, dried, and finished.

I am not aware of any marked improvement in the style of printing called "spirit colours," but in that of "steam colours" considerable advance has been made since 1851, rather, however, in a mechanical and artistic, than in a chemical point of view. Thus, it was owing to certain mechanical improvements that Mr. Robert Kay, calico printer of Manchester, and his workmen, had the honour of obtaining the gold medal at the Paris Exhibition of 1855. The beautiful furniture patterns which he exhibited there were the result, not only of artistic skill, and of improved machinery, by which twenty colours can be printed at once, but also of an invention patented by Mr. J. Burch, of Macclesfield, of which Mr. Kay availed himself with great tact. Of course you must be aware that, in order to produce light shades of colour, the darker shades are diluted with gum-water, or reducing liquid; this was the work of the colour mixer, and, therefore, to produce four colours and four shades of each colour, sixteen rollers would be required. Now the invention of Mr. Burch consists in reducing the colour upon the cloth during the process of printing. The pattern of the paler shades of each colour in a chintz design being engraved on one roller, an impression in gum-water or reducing liquid is given off upon the cloth first, the impression of the other rollers then following in the usual order; where the different colours fall upon the gum-water a lighter shade is produced, owing to the dilution of the colour on those parts, which effect may be still further heightened, by more lightly engraving the corresponding parts of the colouring roller, so that a less quantity of colour shall be given off. The application of this process to furniture styles, first by Mr. Kay, and of late by Messrs. Littlewood and Wilson, and other large calico printers of Manchester, together with the



substitution of the large rollers above mentioned, for block printing, has produced quite a revolution in furniture styles.

Pigment Printing.—This style remained for many years in a dormant condition, owing, first to the difficulty of finding a proper fixing agent, and then to the insufficient variety of pigments, for it was necessary to find a substance which would give the pigment the required consistency, and at the same time cause it to adhere to the cloth. Artificial ultramarine was the first pigment attempted to be printed, and in 1843 india-rubber dissolved in naphtha was proposed as a fixing agent for it, but owing to the danger of fire, and for other reasons, this method was abandoned. In 1847, egg albumen was introduced into this country for the same purpose, but owing to the coarseness of the ultramarine, and its high price, which was about £8 per lb. (it is now 1s. 3d.), the progress of this mode of printing was greatly retarded. In 1849, Mr. R. T. Pattison, of Glasgow, patented the use of caseine from milk, which he called lactarine, which promoted the use of ultramarine, buff, and stone pigments in shawl printing. About the same period another fixing agent was introduced, viz.,

Ultramarine Printing. albumen obtained from blood. The style of pigment printing, however, received an extraordinary impetus in the spring of 1859, when the purple aniline of Mr. Perkin was successfully introduced by Messrs. Black and Co., of Glasgow, and the French purple of Messrs. Guinon, Marnas, and Bonnet, of Lyons, by Messrs. Walter Crum and Co., Dalglish and Co., Boyd and Hamel, Inglis and Wakefield, Heys, &c.,



and the splendid mauves and purples which astonished the world by their beauty, fastness, and brilliancy, were obtained by printing albumen or lactarine on muslin, and fixing the same by coagulating it by the action of steam. The pieces were then passed into the dyebeck, containing in solution Mr. Perkin's aniline purple, or Messrs. Guinon, Marnas and Co.'s French purple, first dissolved in oxalic acid, and then added to a slightly ammoniacal bath, when the albumen or lactarine took up the colour and fixed it on the cloth, the pieces being then thoroughly washed, to remove any excess of colour. In the middle of the same year

*Muslin printed with
French Purple.*



a beautiful green pigment, which had been patented in 1858 by Mr. Guignet, was introduced, and as it is extensively employed, it may be interesting to know how this green oxide of chrome is produced. Three parts of boracic acid are intimately mixed with one part of bichromate of potash and a sufficient quantity of water to form the whole into a thick paste. It is then introduced into a furnace, and heated to a dull red heat, when a borate of potash and a borate of oxide of chrome are produced. The mass is allowed to cool, and is then thrown into cold water, when the borate of potash dissolves, and the borate of oxide of chrome is decomposed. The hydrate of oxide of chromium, $\text{Cr}_2\text{O}_3 + 3\text{H}_2\text{O}$, falls to the bottom as a magnificent green powder, which requires only to be well washed and drained to be ready for use. The peculiarity of this green, as well as of one prepared by Mr. Arnaudon, of Turin, from phosphate of ammonia and

bichromate of potash, is that, besides being of a brilliant green, they maintain this colour by artificial light. In the month of

Guignet's Green.



November, 1859, the magenta colour, or fuchsine, of Messrs. Renard, was also introduced to the printing trade, and fixed by the above described method. The beautiful pinks thus obtained were soon followed by the application of roseine, azaléine, and other aniline reds. In May, 1859, a further improvement was made, which reduced the cost of applying these colours

to muslins, by Mr. Walter Crum, who made the curious observation that if the gluten of wheat flour is allowed by exposure to the atmosphere to fall into a semi-fluid condition, it dissolves easily in a weak solution of caustic soda, which solution he used as a substitute for albumen or lactarine. About the same time, Mr. Scheurer-Kestner also introduced the use of gluten by the aid of weak acids, and Messrs. W. A. Perkin, and Matthew Gray, of the Dalmonach Printing Company, proposed to fix the coal tar colours on fabrics by means of a lead soap.

Early in 1860 calico printers succeeded in printing the aniline colours directly with the animal mordants, instead of dyeing

*Pigment Printing.**



the mordants after the latter were printed and fixed, and thus were enabled not only to print a variety of colours on the same piece, but also to effect a great saving and simplicity in the operation. By this means the pigment style was fully developed, and an entirely new class of prints was introduced into this market.

Owing to the great extension of this style, the cost of the animal mordants employed became such a serious consideration as to cause anxious search for other means of fixing the colours, and Mr. Charles Lowe and myself having observed in 1856 that tanning matters would precipitate and render insoluble certain coal-tar colours, and having further observed, at the end of 1859, that tannin, when printed on cloth and submitted to the action of the steam would become fixed, and serve as a mordant for the coal-tar colours, we took out a provisional specification on the 10th of December, 1859, for fixing the insoluble tanning compound formed by adding a solution of gall-nuts to a coal-tar colour, on cloth prepared with oxide of tin or alumina, or other metallic oxides. For various reasons this patent was not proceeded with, but in the early part of 1861 Mr. Gratrix, with the intelligent and persevering assistance of Messrs. Butterworth and Brooks, of Manchester, succeeded in fixing aniline purples, which, though faster against soap than those printed with albumen, did not so perfectly resist the action of light. The first process used by Mr. Gratrix was, with very slight modification, the same as that described above, but his second process, which I think he preferred, was the following:—He took cloth prepared with oxide of tin, such as is generally used for steam colours, and after having prepared it with a gall-nut solution, submitted it to the action

* This sample, as well as the aniline purple, we owe to the kindness of Messrs. James Black and Co.

of steam, when the tannin became fixed and insoluble; the pieces were then passed through a dunging liquor, washed, and then into a beck containing aniline purple mixed with a little acetic acid. As the bath was gradually carried to the boil, the colour fixed itself on the tannin, and thus produced the print, but as the whites were rather soiled, the pieces were passed into a weak acid bath, or through a weak solution of printing clearing liquor, such as is used for garancine.



Early in 1860, Mr. John Lightfoot also took out a patent to fix colours, especially those from coal-tar, by various means, the chief of which was tannate of gelatine. In 1861 patents were secured by Messrs. Pattison, Miller, and Nathaniel Lloyd, and J. G. Dale. The last of these patents is, in my opinion, one of the best which have been taken out for that purpose, and is successfully worked by Messrs. Littlewood and Wilson, of Accrington. The characteristic feature of this process is the employment of tartar emetic as the agent for fixing the aniline purple on the fabric.



It is to be regretted that the beautiful colours obtained from coal-tar should be exposed to injury in public estimation, owing to certain parties printing them with starch only, by which they are so loosely attached to the fabric, that a slight washing in pure water will entirely remove the colour and leave nothing but white cloth. By such means the reputation of this style of printing is being rapidly destroyed, and these colours, which might otherwise become a valuable addition to the printers' repertoire, are likely to lose altogether the favour of the public. This subject is so important that I cannot refrain from making another remark, viz., that if the use of coal-tar colours were properly encouraged, they would doubtless gradually decrease in price, and this country, instead of being tributary to others for its dyestuffs, would in time become the purveyor of dyeing materials, or of the substances yielding them, to the whole world.

I cannot conclude this paper without calling your attention to the immense extent to which calico printing is carried out, and the wonderful progress it has made. Thus in 1830 about 2,000,000 pieces were printed; in 1851, according to a lecture delivered before this Society by Mr. E. Potter, M.P., the estimated quantity of goods exported was 6,465,000 pieces; and the same authority estimates that in 1857 the export of printed calico amounted to about 27,000,000 of pieces.

