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CANTOR LECTURES.

ON DYES AND DYE-STUFFS OTHER THAN ANILINE.

FOUR LECTURES, DELIVERED BEFORE THE ABOVE SOCIETY,

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

Reprinted from the "Journal of the Society of Arts."

ON DYES AND DYE-STUFFS OTHER THAN ANILINE.

LECTURE I.—Delivered Tuesday, February 7th, 1871.

RED COLOURING SUBSTANCES.—MADDER.

This well-known tinctorial substance may still be considered as the most important of all the dye-stuffs employed by calico printers, owing to the brilliancy of the colours, and their permanence under the action of light and soap, and the wear and tear which fabrics so died can sustain, as well as on account of the variety of shade and colour that can be obtained; one dyeing operation being sufficient to produce pinks, reds, purples, violets, puce, and black; and, notwithstanding the competition that madder colours have met with of late years from aniline dyes, I believe the quantity of madder consumed in England is quite as great at the present day as ever it was.

The employment of madder-root as a dye dates from the most ancient times, as is proved by the Egyptians using madder-dyed fabrics to wrap round their mummies. The Greeks and Romans were acquainted with it under the names of *Erythrodanon* and *Rubia*, and their modes of fixing it on cotton fabrics were the same as those now employed, namely, aluminous salts for producing reds, and salts of iron for purples and blacks.

The plant which produces madder is an herbaceous one, and is called *Rubia tinctorium*. It bears a yellow flower, and a dark red berry fruit. The red colouring matter exists almost entirely in the cortical part of the root, little or no colour being found either in the epidermis or in the ligneous or centre part of the root. M. Decaisne and M. Édouard Koechlin have shown that the colouring matter in the fresh root is yellow, and becomes red under the oxidising influence of the atmosphere. The same process goes on, to a certain extent, in the roots of the plant when they are allowed to remain several years in the ground, especially in chalk formations. In France, the roots are allowed to remain in the ground two or three years; in Turkey and the East, from five to seven. In the latter countries and in Naples, they are dried in the open air, but in Holland and France stoves are employed for this purpose. Naples and Turkey madders are imported in the root, and are known in commerce as Naples and Turkey roots, while those from France and Holland are ground, and sold under the name of French and Dutch madder.

One hundred parts of fresh root yield on perfect desiccation twenty parts of dried substance. The roots as imported always contain sixteen or eighteen per cent. of water; the fresh roots, therefore, give 24 or 25 per cent. of commercial madder. Dutch and Alsacian madder, after being ground, is stored in large casks, and kept for two or three years, when the colouring matter is developed, and its tinctorial power is much increased; if, however, it is kept five or six years, further changes ensue, and its value seriously decreases. French Avignon madder can be employed at once, although the quality is much improved by keeping it one or two years. The best Avignon madders are grown on lime formations. The roots that have a red colour are called *palus*, and those that are pink *rosées;* the former being considered the finest. The value of these madders is in ratio to the fineness of their powder, the finer powder containing the most colouring matter.

The nature of the chemical changes occurring in madder during the time it is stored, and which so much improves its commercial value, was entirely unknown until the elaborate and interesting researches of Dr. Ed. Schunck, F.R.S., published in the year 1851. He succeeded in isolating a peculiar ferment called *Erythrozym*, which possesses the property of decomposing a substance called by him *Rubian*. Rubian may be considered as a glucoside (this name being given by chemists to compounds of sugar with other organic principles), and is decomposed by erythrozym into a peculiar sugar and *Alizarine*. Whether there are in the rubia-root several glucosides which unfold themselves respectively into sugar and one of the colour-giving principles, or there is only one glucoside, and its colour-giving principle as it is liberated gets successively oxidised into alizarine, purpurine, &c., is not yet satisfactorily determined. Still, this valuable discovery of Dr. Schunck has thrown much light on the subject, and has led to several important commercial improvements, to which I shall call your attention as I proceed. One hundred parts of dried madder-root consist of—

Soluble in cold water	55 parts.
Soluble in boiling water, and which contains the greater part of the colour-giving principles	3 ,,
Soluble in alcohol	1·5 ,,
Fibrous matter	40·85 ,,

I shall make no remark on the gum, mucilage, pectine, pectic acid, and pectates which the rubia-root contains, but state that the water extract contains also the yellow colouring-matter discovered by Kuhlmann in 1824, and called by him *Xanthine;* but this colour has never received any commercial application, from its want of brilliancy. Water also dissolves another colouring principle called *Chlorogenine*, which is decomposed by weak acids into sugar and a brownish green matter. Both these

colouring substances are sources of annoyance to the calico printer, as they render very difficult the obtaining of pure whites in printed goods, and they dim the brilliancy of the shades produced by the combination of alizarine and purpurine with the mordants. Further, the cold water dissolves the sugar contained in the root, and on the Continent it is transformed into alcohol. The yield of alcohol varies with the nature of the root, and ranges between 7 and 10 lbs. per cwt. of root. This fact shows that there is from 10 to 15 per cent. of sugar in the root.

Messrs. Julian and Roquet have based on the above facts a commercial process for preparing a purified madder, which they call *fleurs de garance*, of which several million pounds are now manufactured in France per annum. It not only yields brighter colours than the original madder, but, as it does not soil the white parts of prints, its use saves the printer much soap and labour. To prepare the fleurs de garance, the madder is mixed with eight or ten parts of water, and left for three or four days at a temperature of 75 to 80° Fahr., when fermentation ensues, transforming the sugar of the root into alcohol, which is collected. The madder, deprived of all soluble substances, is dried, and ready for use. A hundred parts of madder yield from 55 to 60 per cent. of fleurs de garance. I may state, *en passant*, that the injury which Dutch and Alsace madders sustain when kept too long in casks is doubtless owing to the fact that, after the erythrozymic fermentation is completed, an alcoholic and lactic one sets in, which acts injuriously on the colour-giving principles.

I now proceed to lay before you the outlines of two interesting processes for extracting commercially the two useful colour-giving principles, *Alizarine* and *Purpurine*.

The first is due to M. Leitenberger, and is based on the fact that pupurine is soluble in water at 130°F., whilst alizarine only dissolves at 170°F. He mixes madder with water, and heats the whole gradually, by means of a jet of steam, at 130°, at which temperature it is maintained for some time. The liquor is then run off and filtered. To the clear solution, lime, or, still better, baryta, is added, when a lake precipitates. This is washed and mixed with hydrochloric acid. The purpurine thus liberated is thrown on a filter, washed, and is ready for use. The madder remaining from the above operation is dried and heated in close vessels with wood spirit, which dissolves the alizarine. This extract, thus obtained, after being concentrated by distillation, is ready for use. A hundred parts of root yield from two to three per cent. of purpurine, and four or four and a half per cent. of alizarine.

The second process, that of Professor Emile Kopp, is based on another discovery of Dr. Schunck, namely, that weak acids acts upon rubian in the same manner as erythrozym, unfolding it into sugar and alizarine. M. Kopp found, some years since, that sulphurous acid dissolved the glucosides of purpurine and alizarine, and applied this observation as follows:— 600 lbs. of Alsace madder are macerated for 12 or 15 hours with 800 gallons of a weak solution of sulphurous acid, to which is added one-thousandth part of hydrochloric acid, to neutralise the earthy carbonates existing in the root. This operation is repeated three times. To the liquors, three per cent. of sulphuric acid are added, and the whole heated to a temperature not exceeding 140° Fahr., when red-coloured flakes separate and gradually deposit, which, when washed and dried, are commercial purpurine. The liquor is then carried to the boil for a couple of hours, and allowed to cool, when a dark green powder is found deposited in the vessels, which, when washed and dried, is commercial alizarine.

This process has been carried out by Messrs. Schaeffer and Lauth for many years, and no doubt yields a larger amount of colour-giving principle than M. Leitenberger's method, the glucosides being doubtless more completely decomposed by the acids than by water alone. It

has the further advantage of obtaining the colouring matters free at once, which have only to be washed to be ready for use.

The dyeing power of the alizarine thus obtained is equal to 40 times its weight of madder, or 10 times that of garancine. These colouring substances, except green alizarine, are not substituted for madder in the dyebeck, but are printed on the cloth and steamed, as will be described further on.

M. Kopp found that his green alizarine is a mixture of alizarine with chlorogenine; and that this latter body can be separated by treating the mixture with a light oil of tar, having a boiling point of 300° which dissolves the chlorogenine. Alizarine is employed in the production of rich purples, whilst purpurine is used for reds and pinks.

Before describing pure alizarine and purpurine, I may state as a fact very interesting, although of no commercial value, that if superheated steam be passed over a preparation of madder known as garancine, pure alizarine is volatilised, and may be easily collected.

Pure crystallised alizarine was discovered, in 1824, by MM. Robiquet and Colin, by treating madder with strong sulphuric acid, when they produced a black mass, which they called " charbon de garance," and which, on being heated at a moderate temperature, yielded crystals of alizarine.

In 1851, Dr. Schunck succeeded in isolating from madder a substance to which he gave the name of *rubian*. This he effected by filtering a hot decoction of madder on pure animal black, which is washed with cold water to remove chlorogenine. The washed charcoal is boiled repeatedly with alcohol, and the alcohol solution evaporated to dryness. The dry mass is dissolved in water, and acetate of lead added, which gives rise to a precipitate. This precipitate, when acted on by sulphuretted hydrogen, gives pure rubian in solution. When rubian is acted on, either by erythrozym or weak acids, it is decomposed, yielding, according to Dr. Schunck's paper, alizarine and water; according to M. Schützenberger, alizarine and glucose, or grape sugar.
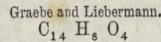
Pure alizarine sublimes, at a temperature of 460° Fahr., into pale orange prismatic crystals. When slowly crystallised from an ethereal solution, it forms a hydrate, containing two equivalents of water, which crystallises in lustrous scales. Cold water dissolves a mere trace of alizarine, but its solvent power increases as the temperature is raised, as may be seen from the following figures:

At 212° 100 parts of water dissolve .... ·034
At 400° ,, ,, ,, ... ·820
At 480° ,, ,, ,, ... 3·160

Alizarine is freely soluble in alcohol, ether, wood spirit, benzole, turpentine, sulphuret of carbon, and glycerine. It is soluble without decomposition in sulphuric acid, even at a temperature of 400° Fahr., and is thrown down unchanged when large quantities of water are added. It is soluble in a warm solution of alum, but insoluble in a cold one. It has been assigned different formula by different chemists, the two most generally adopted being that of Dr. Schunck, $C_{14} H_{10} O_4$, and that of Wolf and Strecker, $C_{20} H_{12} O_6$. Alizarine gives a purple colour with a weak solution of caustic alkali, which undergoes no change by the action of air. It yields, with alumina fixed in fabrics, a variety of red and pink shades; with oxide of iron it gives purples and blacks; and, with a mixture of these two oxides, chocolates.

I shall now call your attention to one of the most interesting and important discoveries of chemistry, as applied to manufactures, which have been made of late years, namely, the artificial production of this most important colour-giving principle, alizarine, or of a substance which, if not identical, has great similarity to it. Messrs. Graebe and Liebermann, and Mr. Perkins, believe in the identity of the artificial product with the natural one. But this is denied by M. Alfraise, on the grounds, first, that the formula given by Messrs. Graebe and

Liebermann does not agree with that given by Dr. Schunck, as is shown by the following figures :—

Schunck.	Graebe and Liebermann.
$C_{14} H_{10} O_4$	$C_{14} H_8 O_4$

Secondly, that the artificial alizarine does not give the same coloured sublimate as the natural alizarine ; and thirdly, that if both these substances are acted on by nitric acid, natural alizarine is converted into phtalic acid, whilst the artificial alizarine, which he calls alizapurine, yields a large quantity of a nitro-compound having an intensely bitter taste, mixed with only a mere trace of phtalic acid. These observations of M. Alfraise have been confirmed by M. Kopp. That the commercial artificial alizarine is not identical with a natural alizarine is rendered still more certain by the researches of Dr. Schunck, who, on examining a sample obtained from Mr. Perkins, found it to contain a large quantity of a compound crystallising in yellow, silky needles, anthraflavic acid, and which he obtained by treating Mr. Perkins's product with alcohol. On treating the acid with fuming nitric acid he obtained a nitro-compound, the potash salt of which he describes as resembling picrate of potash. This is doubtless the bitter principle which Alfraise obtained, but did not study. Dr. Schunck gives the formula of anthraflavic acid as $C_{15} H_{12} O_4$ and considers it homologous to alizarine, one equivalent of its hydrogen being replaced by methyl. Messrs. Graebe and Liebermann, and Mr. Perkins, found their opinion as to the identity of the two alizarines, on the fact that they give the same absorption bands on being submitted to Professor Stoke's spectrum test.

Artificial alizarine was first made in 1869, by Messrs. Graebe and Liebermann. The substance from which they obtain it is *Anthracene*, a body discovered by Professor Anderson, of Glasgow. Anthracene is one of the last products passing over in the dry distillation of coal-tar, and is found most abundantly in the 10 or 15 per cent. which comes over from the temperature where soft-pitch is formed, and that where hard pitch is produced. The quantity of anthracene in coal-tar varies greatly ; it is most abundant in the tars obtained from those coals which yield most naphtha. The South Staffordshire coals give the largest quantity, whilst the Newcastle coals give very little. Its extraction can only be carried on with advantage in cold weather, as it becomes very soluble on a slight rise of temperature in the oily homologues which accompany it. At a temperature of about 40°, the distillate above described is semi-fluid ; it is placed in a hydro-extractor, and the oily fluid separates from the solid matter, which is then submitted to cold and hot pressure. The cake thus formed is pulverised and carefully washed with petroleum spirit, having a boiling point of about 180°, which leaves anthracene moderately pure. This powder dissolved in alcohol and crystallized, yields anthracene in nearly white scaly crystals, or in a fit state for the manufacture of artificial alizarine.

Messrs. Graebe and Liebermann oxidised the anthracene ($C_{14} H_{10}$), by nitric acid, into anthrachinon ($C_{14} H_8 O_2$), this being again converted into bibrom anthrachinon ($C_{14} H_6 Br_2 O_2$), which, by fusion with potash, is changed into alizarine ($C_{14} H_8 O_4$.) There are three patents published, and a process, the details of which are kept secret. It is curious to notice that the patent taken out by the above-named gentlemen and Mr. Caro is dated the 25th of June, 1870, while Mr. Perkins entered his on the day following, in which nearly the same processes are described, merely employing different oxidising agents.

The following is an outline of one of the processes detailed in the specification of Messrs. Caro, Graebe, and Liebermann :—One part of anthracene is heated with four of sulphuric acid, of sp. gr. 1·845, for three or four hours, to a temperature of 212° Fahr., and then for an hour at 300°. The mixture is allowed to cool, and to it is added water equal to three times the weight of anthracene taken, and manganese equal to four times that weight. The whole is boiled for three hours, and a milk of lime is then added, which gives rise to a deposit, consisting of the excess of lime and manganese used, and protoxide of manganese, while there remains in solution a double sulphate of anthrachinon and lime. This solution is now acted on by carbonate of soda in slight excess, carbonate of lime separates, and the salt of soda thus produced is evaporated to dryness. To this solid mass is then added two or three parts of caustic potash or soda and a small quantity of water, and the whole heated under pressure, in suitable vessels, at a temperature of 350° to 500° for one hour, when the anthrachinon is further oxidised, and converted into alizarine. This anthracene, $C_{14} H_{10}$, gives anthrachinon, $C_{14} H_8 O_2$, and this alizarine, $C_{14} H_8 O_4$. The alkaline mass, on cooling, is dissolved in water, and sulphuric or acetic acid added in slight excess, when an orange-yellow flocculent substance precipitates, which, when properly washed and dried, is artificial alizarine.

The second colour-giving principle of madder, to which I have referred several times already, is called purpurine, and was also discovered by MM. Robiquet and Colin, in 1828. Although in commerce it is sold as a red powder, as has been mentioned above, still, by heating at a temperature of 480° Fahr., it can be obtained in the form of feathery crystals, of an orange-red colour. It is more soluble in water than alizarine, especially at a temperature of 140° Fahr., and is also soluble in the menstrua already mentioned under alizarine. Further, it gives a red colour with caustic alkali, instead of purple as alizarine. It is soluble in a cold solution of alum, while alizarine is not. When fixed on fabrics, its colours do not stand exposure to light as well as those of alizarine.

Professor Stokes, of Cambridge, has found a most elegant method of discovering and characterising mere traces of these colouring principles. So delicate is the test, that the colouring matter on one square inch of dyed fabric is sufficient to obtain the results. He treats the fabric with a solution of carbonate of soda, which dissolves the colouring matter. The solution is then introduced into a small tube, which is placed before a slit in the shutter of a dark room. The light which passes through is decomposed by a prism, when a spectrum is produced. The operator will observe that, when purpurine is taken, there are principally two black bands formed by the absorption of light in the green part of the spectrum, having between them a band of green light, whilst alizarine exhibits, on analysis, a band of absorption in the yellow, and another narrower one between the red and the orange.

Professor Schützenberger, by treating commercial purpurine successively with alcohol and benzine, unfolded it into four different substances, to which he assigns the following formulæ :—

Alizarine ...... $C_{20} H_{12} O_6$
1 Purpuroxanthine $C_{20} H_{12} O_6$ or $C_{20} H_{14} O_6$.
2 Purpurine .... $C_{20} H_{12} O_7$ or oxy-alizarine.
3 Orange matter.. $C_{20} H_{16} O_9$ or hydrate of purpurine.
4 Pseudopurpurine $C_{20} H_{12} O_9$ or oxy-purpurine.

I shall now call your attention to a very remarkable discovery, recently made by the late Professor Bolley, viz., the conversion of purpurine into alizarine. If purpurine is heated in the atmosphere, as stated above, it is nearly all sublimed, leaving only a small amount of carbonaceous residue, but if heated in sealed tubes, at a temperature of 400°, it forms a carbonaceous mass from which water extracts alizarine. Under the influence of the high temperature, the purpurine loses an equivalent of oxygen, and is converted into alizarine. This reaction appears to confirm the opinion of M. Decaisne, that the madder plant contains only one colour-giving principle, which under the oxidising influence of the atmosphere becomes converted, first, into alizarine, then purpurine, and afterwards into the still more highly oxidised compounds.

The difficulty and expense experienced by calico-printers in brightening their colours, and obtaining pure whites in madder-dyed goods, attracted many years ago the attention of scientific and practical men, and any process by which these difficulties might be overcome was anxiously looked for. The discovery of MM. Robiquet and Collins, that the colour-giving principle was not destroyed by sulphuric acid, was the step in that direction, and led M. E. Schwartz to observe that the carbonaceous mass of Robiquet, if carefully washed and neutralised, could be used as a dye-stuff. MM. Lagier and Thomas improved upon this, and introduced, in 1839, an article which is now extensively used by calico printers and named garancine, and now is prepared as follows : — Madder, either unwashed, or, better still, washed with cold water, is mixed with one-third of its weight of sulphuric acid, which has been previously diluted with water till it marks 10° Twaddle ; it is then boiled for four or five hours, and the mixture run on to woollen filters, and washed till only a mere trace of acid remains. It is then either removed or washed once with a very weak solution of carbonate of soda, submitted to hydraulic pressure, and then introduced into drying stoves. One hundred parts of madder yield from 34 to 37 of garancine. Garancine is a fine powder of a light brown colour, and has a dyeing power four times as great as the original madder. It does not give as good blacks as madder, nor are its purple, red, and pink so fast, but its purple is brighter, and the whites are obtained pure without soaping, it being only necessary to substitute a slight clearing liquor, composed of an alkaline, hypochlorite of soda, to which is added a small portion of sulphate of zinc.

In 1852, Messrs. Pinckoff and Schunck effected an improvement in the manufacture of garancine, their product being known in England under the name of commercial alizarine; but on the Continent it is better known as *Pincoffine*. Their process consists in submitting ordinary garancine to the action of high pressure steam of a temperature of 300° F., which, whilst it does not act on the alizarine contained in the garancine, destroys two other colouring matters which are present. These Dr. Schunck has isolated and examined, and named *Rubertine* and *Rerantine*. They are of a peculiar resinous nature, and spoil both the whites and the purples, which are fixed along with alizarine in the dyeing process. The employment of commercial alizarine is especially advantageous in the production of purples, which are faster and more brilliant than those produced by ordinary garancine. The cloth also does not require either soaping or cleansing.

M. Pernod has, within the last two or three years, introduced a madder extract, which is at the present time extensively used in Lancashire as a topical colour. This term is applied to a colour which is printed on a fabric, and afterwards fixed by steaming. By this method bright and fast colours are introduced in printed goods, producing much more effective designs than could be effected if the goods had to pass through a dye-beck and afterwards be washed with large quantities of water. Some splendid specimens of this class of printing were to be seen at the last Universal Exhibition, 1867.

To prepare the extract, garancine is lixiviated till completely exhausted, with a nearly boiling solution of sulphuric acid, containing five parts of acid to a thousand of water. On cooling, an orange red precipitate falls to the bottom of the vessel, which, when collected and thoroughly washed, constitutes an extract ready for use. The products of M. Leitenberger and Messrs. Schaaffer and Lauth may be substituted for this extract.

As the employment of these extracts is the most important improvement recently introduced into calico printing, I will give the three following recipes for their application :—To produce dark red, take 8 lbs. of extract of madder, 4 lbs. acetic acid, and 1¼ lbs. starch.

Boil these in an earthenware vessel, and when cold add to six measures of the above one of acetate of alumina and a very small quantity of Gallipoli oil, say 1 per cent. For a pale red, take 4 lbs. of extract of madder, 2 lbs. of acetic acid, 10 quarts of gum Senegal water, and 1 pint of acetate of alumina. To obtain a purple, take 1 pint of extract of madder, half pint of acetic acid, half pint of water, and 3 ozs. starch; boil, and when the mixture is cool, 5 ozs. measure of acetate of iron of 24° Twaddle, and 5 ozs. of water. To produce a chocolate, proceed as in the last recipe, substituting acetate of chrome for the acetate of iron.

The above mixtures are printed on cloth by means of engraved copper rollers, and are then dried and submitted to dry high-pressure steam for one or two hours, when the colours have become fixed on the fabric. After being slightly soaped, to remove all excess of colour, the prints are stiffened, and ready for the market.

Although I have now concluded my lecture on madder as a dye-stuff, and have already exceeded the time allotted to me, I hope you will allow me a few minutes more, to enable you to give an outline of the processes by which madder styles are produced, the more so as there may be some persons present who are not aware how madder and garancine prints, now manufactured in such enormous quantities and in such general use, are produced.

To effect this, the ordinary white calico, as sold in shops, is not sufficiently deprived of its impurities to be employed in madder or garancine styles; it has therefore to undergo further bleaching operations. The calico so extra bleached is then printed by means of copper rollers, on which the pattern to be produced is engraved. This roller leaves on the calico a red, purple, or chocolate mordant; that is, for red, a sulpho-acetate of alumina, or red mordant ; for purples, violets, and blacks, an impure acetate of protoxide of iron, known in the trade as pyrolignite of iron, or black liquor ; and for chocolates a mixture of these two mordants.

After this operation the pieces undergo a process technically termed ageing. This was formerly effected by spreading out the pieces, and hanging them in a room for three or four days, so that the acetate of alumina might lose part of its acetic acid, and the iron mordant nearly the whole of it, thus liberating the oxide of iron and enabling it to undergo partial oxidation.

Some few years ago, Mr. David Thom introduced a process by which this is effected in twenty minutes; it consists in passing the printed mordanted cloth over rollers fixed in a machine placed in a chamber about twenty feet long, in which a current of air and steam is thrown. The temperature of this chamber must not be below 100° nor above 108°, and the quantity of steam present must be such that fifty yards of calico will take up one ounce of moisture during the twenty minutes it takes to pass through the chamber. The printer is able to test the state of the chamber by means of wet and dry bulb thermometers. The next operation to which the cloth is submitted is dunging. The process received this name because formerly the calico was passed through a mixture of cow-dung with water. Now, however, silicates or arseniates of soda, mixed with a little chlorate of potash, are substituted. After passing through either of these solutions they are washed, and ready to be passed through the dye-beck. This beck contains water, and from five to seven pounds of madder, or one to two and a half pounds of garancine, or commercial alizarine, for each piece of calico to be dyed. The heat of the bath is then gradually raised, by means of a jet of steam, to 180° for garancines, or 212° for madders. This operation takes from one and a-half to two hours, according to class of goods, style, &c. The fabrics are then washed and passed through a cleansing liquor for garancine or commercial alizarine styles, or soaped twice at 180° when they are dyed with madder.

The most permanent and brilliant colour produced from the rubia plant on cotton fabrics is Turkey red.

The details so essential to success in dyeing this colour are kept by each dyer a secret, but I will attempt, as briefly as possible, to give the main features of the process. After the bleaching of the fabric is completed, they are passed through Gallipoli oil, and then exposed to the atmosphere in heated chambers. This operation is repeated several times. The next one consists in passing the cloth through a weak alkaline solution. After this they go through a solution of acetate of alumina, and then through a bath of a tannin substance. By these processes, no doubt, the fatty acids of the oil combine with the alumina, as does the tannic acid of the tannin matter, helping to fix the mordant in the fibre of the fabric. On being dyed, the goods assume a rich, dark red tone, to which brilliancy is imparted by passing the dye fabric through heated soap solutions.

I should occupy too much of your time were I to attempt to enter into the details of the methods by which chemists determine the relative tinctorial powers of roots, madders, and garancines, but I may give you a very simple method of detecting ordinary adulterations of garancine by dye woods and tannin matters. Pieces of blotting paper are dipped into a weak solution of chloride of tin and sulphate of protoxide of iron, and on each of these sheets is sprinkled a little of the suspected garancine. If a dye wood be present, the chloride of tin paper will assume a red colour, and if tannin matter be present, the iron paper will be blackened.

LECTURE II.—Delivered Tuesday, February 14th, 1871.

RED COLOURING SUBSTANCES (*continued*).—MUNJEET; CAMPECHY, PEACH, SAPAN, CANE, AND BAR WOODS; ALKANET ROOT; SAFFLOWER; COCHINEAL, LAC DYE; MUREXIDE.

Munjeet.—It is to the researches of Dr. John Stenhouse, one of the most eminent and learned of English chemists, that we are indebted for our knowledge of the true composition of many of the dye-stuffs, and it is to him that we are indebted for the whole of the information we possess in the colouring matters of munjeet, or *Rubia munjista*.

This peculiar variety of the genus rubia is cultivated exclusively in Asia, and especially in India, where it has been used as a dye-stuff for a long period of time, either alone or mixed with other dyes, to produce a variety of red shades. It is imported into this country from time to time, but has never been extensively used, as the colours produced from it are neither so fast nor so bright as those obtained with *Rubia tinctorum*.

Whilst the colouring principles of madder are purpurine and alizarine, those of munjeet are purpurine and a yellow colouring matter, named by Dr. Stenhouse munjistine. He has assigned to this latter body the formula $C_{16} H_8 O_6$. When crystallized from an alcoholic solution, it forms large, beautiful, golden-coloured flakes, which sublimed, give prismatic crystals of an orange-red colour. It is only slightly soluble in cold water, but freely soluble in hot water. Its best solvent is bisulphuret of carbon, which was employed with success by Dr. Stenhouse in separating the purpurine and munjistine from the other substances existing in munjeet. He states that the munjeet root contains as much colouring matter as the *Rubia tinctorum*, and, according to Mr. Higgins, of Manchester, it yields from 52 to 55 per cent. of a garancine; but as it has only half the dyeing power of ordinary garancine, it cannot be employed with advantage for this purpose. The inferiority of munjeet arises from its containing only the comparatively feeble colouring matters, purpurine and munjistine. Munjeet is not much used by calico printers, as the munjistine gives a brownish-purple with salts of iron, which prevents it being employed with that mordant. It is used for special shades of Turkey red, the munjistine giving, with salts of alumina, an orange-yellow colour, which is in some instances employed by the dyers.

I have now the pleasure of calling your attention to an important class of dyeing substances, "the dye-woods."

Campechy or Logwood.—This wood, obtained from a large tree of the leguminous family, called by the botanist *Hematoxylum campechianum*, grows abundantly in the West Indies, Mexico, and other states of South America. The best quality is imported from the Bay of Campechy, in the Gulf of Mexico. Large quantities are also obtained from Jamaica and St. Domingo. The qualities obtained from Honduras, Martinique, and Guadaloupe are inferior.

Campechy was introduced into Europe by the Spaniards, but it was not till the reign of Elizabeth that it came into use in England, and then only for a short period, after which its employment was forbidden under the severest penalties for upwards of a century.

The discovery of its colouring principle, hematine, was made in 1810, by my learned and venerable master, M. Chevreul (who, although now 85 years old, is still actively engaged in scientific pursuits). Shortly afterwards it was studied by Ermann, who gave it the name of hematoxyline. It was obtained by these eminent chemists as yellowish white prismatic crystals, which become discoloured by contact with the oxygen of the air and the small amount of ammonia which the atmosphere contains. It is only slightly soluble in cold water, but much more so in hot. It is very soluble in alcohol, ether, and bisulphuret of carbon. It combines with three equivalents of water, forming a crystalline hydrate, which at 212° F. retains one equivalent.

Hematine in the presence of oxygen, especially under the influence of alkalies, assumes a beautiful purple colour. This colouring matter can be obtained under the form of purple-black crystals, having a metallic lustre, and has received the name of hemateïne. Hematine has the formula $C_{16} H_{14} O_6$, which, on conversion into hemateïne, becomes $C_{16} H_{12} O_6, H_2O$. The hydrate is $C_{16} H_{14} O_6, 3 H_2O$, which at 212° F. becomes $C_{16} H_{14} O_6, H_2O$.

The oxydation, and consequent colouration, of hema-

line under the influence of oxygen and alkalis is so rapid that it may be used as a most delicate test of the presence of carbonate of lime in natural waters; and it is a fact well-known to practical dyers, that waters containing a large quantity of carbonate of lime are well adapted for the production of good log-wood blacks. Hematine gives little or no colouration with salts of protoxide of iron, but hematëine gives a dark purplish blue; the latter also gives dark blue precipitates, with salts of lead and tin. Hematëine is easily reduced to hematine by hydrogen and sulphuretted hydrogen.

In my opinion, the colouring matter in *Hematoxylum campechianum* exists in the state of a glucoside, for when the trees are felled the wood is colourless; but by the time the logs arrive here the outside is of a dark red colour, whilst the inside has only become of a pale yellow colour.

As hematëine is the principle which the dyer requires, the logs are ground into a coarse powder, which is moistened and laid in beds 15 or 20 feet long by 10 or 12 broad, and about three feet thick. A slow fermentation ensues, by which the glucoside is decomposed and the hematine liberated. It is converted into hematëine by stirring the mass, thus exposing it to the oxygen of the air, the action being quickened by the ammonia of the atmosphere as well as by that given off by the decomposition of the azotised principles existing in the wood.

This prepared wood is used by the dyer to produce log-wood blacks, as I shall describe further on, and also by wood extract manufacturers, who prepare an extract which is much used in calico printing. To prepare this extract it is necessary that the wood should not be too highly oxidised, and that the solution obtained from it by successive and repeated lixiviation should be slowly concentrated at a comparatively low temperature, that is to say, not exceeding 150° F.; for if a high temperature be employed the hematëine is still further oxidised, and a dark purple resinous principle produced, which spoils the brilliancy of the colour.

This extract is chiefly used in print works, to produce purples in steam styles.* A strong log-wood solution is thickened with starch, and printed on a prepared cloth; that is, a cloth that has been passed through a solution of stannate of soda, then through weak vitriol, by which means the binoxide of tin has been fixed as a mordant in the fibre of the cloth; the fabric, after washing and drying, is ready for the printer. After being printed, the cloth is either rolled on a perforated cylinder or hung in an iron chamber, and submitted to the action of steam, when the hematëine combines with the oxide of tin, producing a beautiful purple.

If blacks are to be produced, an iron mordant is fixed on the fabric, which is then passed through a logwood solution. It is afterwards washed, and the black fully developed by passing it through a hot dilute solution of bichromate of potash.

Log-wood and its extract are much used in Yorkshire for producing cheap blacks on mixed fabrics, which are goods in which the warp is cotton and the weft woollen. The black is produced by dyeing the fabric in a bath composed of logwood, sulphate of soda, and bichromate of potash.

It is often very useful to distinguish logwood blacks from sumach and other fast blacks, and logwood purples from aniline purples. This is easily effected by submitting the piece to the action of weak acids; the logwood colours assume a bright red tint, while the others remain unchanged.

Brazil Wood.—We shall now pass on to a series of woods which are all obtained from the genus *Cesalpinia*, belonging to the natural order *Leguminosæ*.

Although these woods have long been employed as

dyes by the natives of the countries where they grow, it is only since the introduction of Brazil wood by the Spaniards that their value as dye stuffs has been known in Europe. The best qualities are all imported from Brazil. The particular wood known as Brazil wood, derived from the *Cesalpinia braziliensis*, has become scarce in the market, from its having been all cut in the districts within easy distance of shipping ports.

The wood most in favour at the present day comes from Pernambuco, and is the *Cesalpinia Christa*. This tree is also found in Jamaica. That obtained from Sierra Nevada is not of such good quality.

Another variety, bearing the name of peach-wood, is chiefly derived from Nicaragua. A third, known as Sapan-wood, comes principally from Siam, the East Indies, and other eastern countries. A rather inferior quality, known as Lima-wood, is imported from Peru.

All these woods appear to contain the same glucoside, and, like the previous ones, are decomposed by peculiar ferments, into a saccharine matter and a colour-giving principle. This is proved by the following experiments. If the decoction obtained by treating the wood from the interior of the sticks be boiled with a solution of double tartrate of potash and copper (the best known test for grape sugar), no precipitate is obtained; while if the glucoside be first decomposed by boiling with a dilute solution of hydrochloric or sulphuric acid, and afterwards treated with the copper salt, an abundant precipitate of suboxide is thrown down. The decoction, which has only a faint yellow colour, gives a most abundant and brilliant precipitate with subacetate of lead. The colour-giving principle was discovered by M. Chevreul, who gave it the name of *brazilïne*. By oxidation it is converted into *brazilëine*. It also combines with water, to form a hydrate containing two equivalents of water. Professor Bolley gives the formula of braziline as $C_{22} H_{20} O_7$, and that of the hydrate $C_{22} H_{20} O_7, 2 H_2 O$. He has also made the curious observation that a comparison of the formulæ of hematine and braziline shows a difference equal to carbolic acid, as may be seen by the following table:—

$$\text{Braziline} \quad C_{22} \ H_{20} \ O_7$$
$$\text{Hematine} \quad C_{16} \ H_{14} \ O_6$$

$$\text{Difference} \ C_6 \ \ H_6 \ \ O_1 \ \text{Carbolic acid.}$$

What is still more remarkable is, that by the action of nitric acid upon hematine, he obtained oxalic acid, whilst under similar circumstances braziline yields oxalic acid and picric or trinitrophenic acid, which is the product obtained when carbolic acid is acted upon by nitric acid.

A decoction of any of these woods becomes yellow or orange, (according to the quantity of braziline or brazilëine it contains) on the addition of an acid, and by the addition of an alkali, a beautiful crimson red, the shade of which varies according to the proportion of the two principles. It also becomes red with bichromate of potash, and gives a red precipitate with oxymuriate of tin.

These characters are sufficient to distinguish between a solution of these woods and one of log-wood.

To prepare a good commercial extract from these woods, they must be finely ground, as they yield their colour to water with difficulty; like log-wood, they must be allowed to ferment and oxidise in the air, but not to the same extent. The concentration of the decoctions differs from that of logwood in the fact that they can bear a higher temperature. The more quickly they are evaporated the brighter are the colours which the extract gives. Dr. Dingler has proposed a process which is stated to give very good results. It consists in adding 4lbs. of gelatine, dissolved in water, to every cubic yard of ground-wood, and allowing the whole to ferment for several days. The wood so treated yields a stronger and richer extract than that obtained by the ordinary process; no doubt the gelatine helps the decomposition of the glucoside, and the ammonia produced facilitates

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* Calico printers employ the word style or govels when speaking of a class of goods which are denoted by a word characterising the colouring matter used, or the method employed in producing them. Madder goods and garancine styles may be given as examples of the first and steam styles of the second.

the oxidation of the braziline. By the addition of a small quantity of chlorate of potash to the hot extract, Mr. Peak greatly increased its briliancy, and rendered it more valuable to the printer on account of the brighter colour produced on the fabric.

These extracts are principally used to obtain pinks and reds in steam styles. To effect this, acetate of alumina, chloride of tin, oxalic acid, or acetate of copper is added to the extract, and printed on the prepared cloth already described, which is then submitted to the action of steam.

These woods are also used in conjunction with a little quercitron, or bark, in the production of cheap garancine styles. These inferior garancine prints are easily distinguished from the good ones by means of a hot soap-bath, which only slightly affects the good, while the inferior are almost entirely destroyed. The woods also are sometimes used for the adulteration of garancine.

I may state, before leaving this subject, that the decoction of these woods yield very beautiful pink lakes, which are principally used by paper-stainers.

Common red-ink is also prepared by adding a little alum and acid to an aqueous solution of these woods.

Sandal, Cam, and Bar Woods.—The next class of dye-stuffs which we shall have the pleasure of studying together are derived from several varieties of the genus *Pterocarpus*, which are indigenous to the tropical parts of both the new and the old world. It is principally from the East Indies, Ceylon, Madagascar, and the coast of Malabar, that santal, sandal, or red sanders wood is imported, whilst cam and bar woods are procured from Sierra Leone.

The colour-giving principle of this class of plants is only developed with age, the young branches not containing any, whilst it is found in large quantities in the trunk. Professor Bolley proved that it is the same colour-giving principle which exists in each variety, and he gave it the name of santaline. MM. Wagermann and Haeffely consider that it has the formula $C_{15} H_{14} O_5$. It is a bright red crystalline powder, insoluble in water, but soluble in alcohol, ether, and acetic acid. The latter solvent yields the colouring matter to albumen, which is an important fact, and may one day be rendered practically useful. Santaline is freely soluble in alkalies, giving a violet-red solution, from which acids precipitate the colouring matter.

Sandal-wood is chiefly used on the Continent, where it is employed to give a bottom* to cloth which is to be afterwards dyed with indigo. By this process a very fine blue is produced, having a purple hue by reflected light.

Cam-wood, and especially bar-wood, is chiefly used in England for producing on cotton-yarns brilliant orange-red colours, known as mock Turkey-reds. They are, however, neither so fast nor so bright as the real Turkey-red produced from madder, and are easily distinguished from it by yielding their colour to a hot soap solution, or to alkalies.

Alkanet.—The root of the *Anchusa tinctoria* contains a beautiful red resinous principle, to which Professor Bolley assigns the formula $C_{35} H_{40} O_8$, which is insoluble in water but soluble in alcohol, ether, and bi-sulphuret of carbon. To all these solvents it communicates a fine purple colour, which becomes blue on the addition of an alkali. It is not at the present day employed as a dyestuff, its chief uses being in pharmacy to colour medicines; in perfumery, to colour oils and greases; and in domestic life to give a tint to the lime-wash used for the walls of private dwellings.

Safflower.—Although this dye-stuff has lost much of its value since the discovery of the aniline colours, it is still extensively used in Lancashire for the production of peculiar shades of pinks for the eastern markets. It is

* This term is used in dyeing, to denote that a colour is applied to a fabric with a view of giving a peculiar hue to a dye which is applied after it.

also used for dyeing red tape, and I know no more striking instance of red-tapeism than the love which is shown for this particular dye by the users of this article. Much cheaper pinks can be produced from aniline, and, notwithstanding that many times the attempt has been made to introduce them, it has in every instance failed, because the exact shade has not been attained.

Safflower is the bloom of a peculiar thistle called *Carthamus tinctorius*, which is cultivated in France, Egypt, Spain, Italy, and India. In France and Spain, the small flowers composing the heads of the thistle are picked off and dried in the shade, whilst in Egypt and India they are squeezed, washed with cold water to remove useless materials, slightly pressed into lumps, and dried in the shade; the latter have about double the value of the former. The safflower so prepared only contains three to six parts per thousand of the colour-giving principle.

This principle has received the name of carthamic acid, and has the formula $C_{14} H_{16} O_{14}$. A solution of this acid, when dried on a polished white surface, leaves a varnish, having a beautiful red colour, by transmitted light, whilst it assumes the irridescence of cantharides when seen by reflected light. It is insoluble in water and ether, but soluble in alcohol. This solution becomes yellow on the addition of sulphuric, nitric, or hydrochloric acid. It is also turned yellow or orange by weak alkalies, and the colouring matter in this latter solution, undergoes rapid alteration if exposed to the atmosphere. It is owing to the fugitive nature of the colour, and its easy modification by acid and ammoniacal vapours, that the delicate pinks produced from safflower have been so successfully replaced by the pink aniline dyes.

To prepare carthamic acid, safflower is introduced into bags and washed, till a yellow colouring matter which it contains is removed. It is then mixed with water, to which is added 15 per cent. of the weight of safflower taken of crystalised carbonate of soda. After two hours maceration, the liquor is run off, and cotton yarn dipped in; then lemon juice or citric acid is added to liberate the carthamic acid, which fixes itself on the yarn. Up to this point, the process is the same as that adopted in dyeing fabrics, but to obtain the acid, it is necessary to treat the washed cotton a second time with carbonate of soda, which dissolves out the carthamic acid, leaving a second yellow colouring matter fixed on the cloth. The carthamate of soda thus obtained is decomposed by tartaric acid, and the carthamic acid falls as a brilliant red amorphous powder, which, when mixed with a little water, is sold as safflower extract, and when dry and mixed with ground-talc, is employed as *rouge* by ladies.

There is a particular extract extensively used in dyeing, the preparation of which is a secret. Its value depends on the fact that the carthamic acid is rendered soluble in water.

Cochineal, Kermes, Lac-dye, and Murexide.—I shall now call your attention to four colours derived from the animal kingdom, namely, cochineal, kermes, lac-dye, and murexide.

The first three are distinct species of a peculiar tribe of insects called *Coccina*. The females, from which alone the colouring-matter is derived, form a mass nearly destitute of limbs, and remain attached to one spot on the plants infested by them. The males, on the contrary, are very minute and really elegant creatures, furnished with a single pair of filmy wings. The real cochineal is called *Coccus cacti*; kermes, *Coccus illicis*; and lac-dye, *Coccus lacca* or *ficus*. They all contain the same colouring principle. Although the dyes derived from some species of these insects were well-known to the ancients, and were much used in Persia and India, the true cochineal has only been known in Europe since the discovery of America by the Spaniards; and since the year 1830 only has it been propagated in the Canary Islands, the island of Teneriffe, Java, and Algiers. The best qualities are still obtained from the republic of Honduras.

The *Coccus cacti* lives on a species of cactus called the

Cactus nopal or *Opunta coccinilifera*. This plant is indigenous to Mexico, where it grows in the wild state; and from it large quantities of cochineal are collected. It is also extensively cultivated by the native Indians, who often have plantations containing 60,090 plants. The cochineal obtained from the two sources is of different quality; that from the cultivated plant is much superior, and is called *mestique;* that collected from the wild plant is called *sylvestra*.

I will now explain, in a few words, how cochineal is propagated and prepared for market. In the month of May, in the flat lands, and in November in the mountainous districts, the Indians take the stems of the cactus, which they have preserved from a previous crop, and remove from them the young female insects, which are placed on the growing plants, where they grow and multiply with great rapidity. After a period of about three months, the insects are collected into small tin dishes, so formed as to enclose the bottom part of the plant, and by means of a small brush they are swept from each stem successively into it. They are then destroyed, either by being thrown into hot water and afterwards dried in the sun, or in stoves, which gives the black cochineal, called *zacatilla* or they are placed in a bag and stoved at once, which leaves upon them that peculiar lustrous appearance which characterises the silver white cochineal, called *blanco*. Although one pound of cochineal contains 70,000 insects, there are millions of pounds imported into Europe every year.

If one of the dried insects be placed in warm water it swells, and takes a hemispheric form, when its structure can be seen. If it is pressed between the fingers, thousands of little red grains are exuded, which, if placed under the microscope, are seen to be minute cochineal insects.

The colouring principle was first isolated in an impure state by Pelletier, who considered it to be an azotised compound. MM. Arppe and Warren de la Rue, however, found that it contained no nitrogen, and that it had the formula $C_{14} H_{14} O_8$. As it had distinctly acid properties, they gave it the name of *carminic acid*. M. Schützenberger proved that carmine is composed of carminic acid and an organic azotised base, called *tyrosine*.

MM. Arppe and Warren de la Rue obtain crystallised carminic acid by the following process. The cochineal is treated with ether, to remove fatty matters, then boiled in water. An acid acetate of lead is added to the solution thus obtained, which precipitates an insoluble carminate. This, after being washed carefully, is decomposed with sulphuric acid, the carminic acid being liberated. The aqueous solution is evaporated to dryness, and the mass treated with alcohol, which, on evaporation and cooling, yields it as a crystalline mass.

As shown by the above process, carminic acid is insoluble in ether, but soluble in water and alcohol. It is dissolved without decomposition by concentrated sulphuric and hydrochloric acids. Carminic acid yields on fabrics, especially on wool, one of the fastest colours known, light and air having no action on it. Chlorine alone, easily destroys it. An aqueous solution of the acid gives the following characteristic reactions. With caustic alkalies, it gives a beautiful crimson-red colour; with oxy-muriate of tin, it gives a red precipitate; and with cream of tartar or oxalate of potash, an orange-red precipitate. Alumina removes the whole of the colouring-matter from an aqueous solution. As cochineal is an expensive dyestuff, it is subject to much fraud and adulteration. One of the most common frauds is practised at Nismes and other places where perfumery is largely prepared. The cochineal in those localities is put into water for a short time, by which a part of its colour is extracted; it is then dried, and either sold as black cochineal, or placed in a sack and shaken with talc or sulphate of lead, and sold as white cochineal. This fraud is easily detected by grinding the cochineal and mixing it with water, when the talc or sulphate of lead falls to the bottom. Good cochineal does not leave above five or six per cent. of ash.

It is often advisable before buying cochineal to determine its tinctorial power. This may be ascertained by two or three methods. In the first, equal weights of the cochineal to be assayed, and of one of known value, are treated with alcohol or a solution of alum. The solutions thus obtained are poured into tubes, and placed in a colorometer. This is an oblong box, which has two apertures at each end and two on the top, in a direct line with the end apertures. The tubes are placed through the openings on the top, and, on looking through the end apertures, any difference in intensity of colour between the two liquids can be observed. If a difference is detected, alcohol or water is added to the stronger liquor until there is perfect uniformity of tint. According to the amount of dilution required is the relative value of the cochineals.

A good process was published by the late Dr. Penny, of Glasgow. It consists in exhausting a gramme of cochineal with 50 grammes of potash solution, and this extract is further diluted with 100 grammes of water. The solution thus obtained is mixed with a graduated solution of ferricyanide of potassium (one gramme of salt to 200 grammes of water) till its colour changes to a dark brown. A solution of bleaching powder of known strength can also be used for the same purpose. The best method consists in dyeing equal surfaces of flannel in a bath composed as follows:—

For Scarlet Tints.

	grammes.
Water	1,250
Cream of tartar	2
Tin composition	2
Cochineal	1

For Crimson Tints.
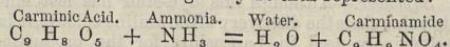
	grammes.
Water	1,250
Cream of tartar	0·75
Alum	1·50
Cochineal	1

The pieces are then washed and dried, and by a comparison of the relative intensity of shade the value of the cochineal is determined.

The chief employment of cochineal is for dyeing wool, but it is also employed in calico printing to produce pinks and reds in steam styles.

It will no doubt be interesting to you to know how to determine whether a pink has been produced from a dyewood, a cochineal, or from madder. All these colours are destroyed by chlorine or bleaching-powder. A boiling soap solution destroys the wood pinks, communicates a crimson hue to the cochineal dye, and brightens the madder colour. Dipped in a rather dilute solution of hydrochloric or sulphuric acid, fabrics dyed with cochineal are not affected, while those dyed with madder or woods assume a yellow tint, which becomes purple when placed in milk of lime. These cloths, however, if subsequently soaped, will yield their colour if dyed with wood, but not if dyed with madder.

Ammoniacal Cochineal.—When one part of ground cochineal is left in contact with three parts of ammonia for several weeks, a chemical action ensues, by which the ammonia loses one equivalent of hydrogen, which unites with an equivalent of oxygen of the carminic acid, giving rise to water and an amide compound, carminamide. Adopting M. Schützenberger's formula for carminic acid, the change may be thus represented:—

$$\underset{\text{Carminic Acid.}}{C_9 H_8 O_5} + \underset{\text{Ammonia.}}{N H_3} = \underset{\text{Water.}}{H_2 O} + \underset{\text{Carminamide}}{C_9 H_9 N O_4}.$$

This compound is also used for dyeing, but before employing it for this purpose, it is necessary to add 4 per cent. of alumina, in the state of jelly, to the mixture described above. The mass is then slowly evaporated to

the consistence of a thick paste. By this means all excess of ammonia is expelled. This preparation is used for dyeing silk, and to produce violet and mauve colours on woollen goods.

Carmine Lakes.—These very beautiful pigments are prepared from a decoction of cochineal, and not from carminic acid, the animal matter which the insect contains, appearing to be necessary to their production. The mode of preparing the finest qualities is kept a secret by the manufacturers; but I will describe two processes, which give very satisfactory results. The first consists in boiling one pound of ground cochineal with two gallons of water, to which has been added one ounce of alum. It is then boiled for three minutes, the liquor is allowed to settle, and, after having been kept for several days, about an ounce of a bright carmine lake is produced. For the alum employed in this process cream of tartar can be substituted. The second process consists in boiling for three hours, two pounds of powdered cochineal in thirty gallons of water. To this is added three ounces of pure saltpetre. The liquor is then boiled again and left to settle. The clear liquor is run off, and after two or three weeks' yields a fine carmine lake.

As these lakes are expensive, they are often adulterated with starch, kaolin, vermillion, &c. The complete solubility of pure carmine lakes in ammonia affords a ready means of detecting these adulterations.

Kermes.—This colouring matter is also derived from a variety of *Coccina*, which lives on the species of oak called *Quercus coccifera*. The young female animal fixes itself under the epidermis of the leaves or young shoots of the oak, in the early part of spring. As the insect grows, it gradually swells out the epidermis, covering the surface of the leaves or branches with a multitude of excrescences. During this period it deposits its eggs.

In Spain and the South of France, during the month of June, or just before the eggs produced would be hatched, the animals are removed, and destroyed by placing them in the steam from heated vinegar.

Although this colouring-matter is seldom used in England, it is extensively employed in the South of France, in Spain, Morocco, and Turkey, to dye morocco leather, and to dye woollen cloth with that particular shade which characterises the cap called "fez," worn by the Asiatics.

If the colour is not so brilliant as that of cochineal, it has the advantage of not being changed by soap or dilute alkalies. It is also employed at Milan, Rome, and Florence to colour a very favourite beverage known as alkermes. The colour-giving principle of this insect is identical with that of cochineal, and has been used as a dye in the East from time immemorial.

Gum-lac.—This is another variety of the *Coccina*, which lives especially on the *Ficus*, or fig tree. They reproduce themselves with such rapidity and in such numbers that they entirely cover the surface of the branches of the trees on which they are deposited. Owing to a resinous fluid which they secrete, they form solid masses, which are often a quarter of an inch thick, all round the branches, and adhere very firmly to them. The natives break off these branches just before the hatching season of the animal, and expose them to the sun to kill the insect. These gum-lac twigs are sold under the name of stick-lac. Those of Siam are considered the best, those of Assam next, and those from Bengal the worst.

There are three kinds of lac in commerce—stick-lac, which has just been described, seed-lac, and shell-lac. The resinous concretion is taken from the twigs, coarsely powdered, and triturated with water in a mortar. The greater part of the coloring principle is thus dissolved.

The granular portion which remains is dried in the sun, and constitutes seed-lac. Shell-lac is obtained by melting seed-lac, and straining whilst hot. It is then dropped upon smooth stems of the banyan tree, and so runs into thin plates, which are known in commerce under the name of shell-lac.

These three lacs have the following composition:—

	Stick-lac.	Seed-lac.	Shell-lac.
Resin	68·0	88·5	90·9
Colouring matter	10·0	2·5	·5
Wax	6·0	4·5	4·0
Gluten	5·5	2·0	2·8
Foreign matters	6·5	..	..
Loss	4·0	2·5	1·8
	100·0	100·0	100·0

The colouring matter of the insect is identical with that of cochineal and kermes, and it has been employed as a scarlet dye-stuff in the East, from time immemorable.

Lac-lake and Lac-dye are preparations imported into this country from India since 1796. They are both prepared by acting on stick-lac by a weak alkaline solution, to which is then added a solution of alum. This produces a precipitate, which, when washed and dried, is ready for use. Although both these lakes are prepared with the same substances, lac-dye is considered much superior in quality. This is due to the greater care bestowed on its preparation. The details of the process are kept secret.

To dye woollen cloths with them, they are dissolved in a weak solution of vitriol, to which is added a little oxy-muriate of tin, and the cloth dipped in when the liquid is near the boil. It only requires washing and finishing to be ready for market.

Some years ago, Messrs. E. Brooke and Co., of Manchester, introduced a lac-dye much superior to that imported from India, which they prepare by treating stick-lac with weak ammonia, and adding chloride of tin to this solution, when a fine red precipitate is formed, which, collected, is ready for use.

Murexide or Roman Purple.—Although this colour has now been superseded by those derived from coal-tar, I call your attention to it as an example of the assistance rendered by the progress of chemistry to the art of calico-printing.

In 1776, the illustrious Swedish chemist, Scheele, discovered *uric acid* in human urine. In 1817, Brugnatelli found that nitric acid transformed uric acid into a substance which he called *erythric acid*, but which was afterwards named by Wöhler and Liebig *alloxan*. In 1818, Dr. Prout found that this latter substance gave, when in contact with ammonia, a beautiful purple red colour, which he named *purpurate of ammonia*—the product known by the name of *murexide* since the researches of Liebig and Wöhler in 1857. These discoveries remained dormant in the field of pure science until the year 1851, when Dr. Saac observed that when alloxan came in contact with the hand it tinged it red. From this he inferred that it might be employed to dye woollen fabrics red, and further experiments showed that if woollen cloth, prepared with a salt of tin, were passed through a solution of alloxan, and then submitted to a gentle heat, a most beautiful and delicate pink colour was obtained.

In 1856, MM. Depouilly, Lauth, Meister, Petersen, and A. Schlumberger, applied it as a dying material to silk and wool, and succeeded in producing red and purple colours, by mixing the murexide with corrosive sublimate, acetate of soda, and acetic acid.

For printing upon cotton, a mixture of murexide with nitrate of lead or acetate of zinc, properly thickened, was printed on the fabric, which was then allowed to dry for a day or two, when the colour was fixed by passing them through a mixture of corrosive sublimate, acetate of soda, and acetic acid.

The uric acid required for the preparation of such large quantities of murexide, was obtained from Peruvian guano. The guano was treated with hydrochloric acid, and washed. The insoluble mass was then treated with nitric acid of specific gravity 1·40. When the action of the acid was completed, the mass was treated with warm water to dissolve out the alloxan. It was then carefully evaporated to such a degree that it became solid on cooling. The solid mass had a brown or violet colour.

LECTURE III.—Delivered Tuesday, February 21st, 1871.

BLUE COLOURING SUBSTANCES.—INDIGO, ORCHIL, CUDBEAR, LITMUS, PRUSSIAN BLUE, AND ULTRAMARINE.

Indigo.—This most valuable dyeing substance was used as a dye-stuff in India and Egypt long before the Christian era, and the Romans were acquainted with it, although they only used it as a pigment, not knowing how to render it soluble, and so available for dyeing. It is only since the sixteenth century, or from the time of the discovery of the passage to India round the Cape of Good Hope, that it has become generally known in Europe; and its employment as a dye was greatly retarded by the opposition it met with from the large vested interests of the woad cultivators, who induced the English, French, and German governments to promulgate several enactments against its use. So severe were some of them, that Henry IV. of France issued an edict, condemning to death any one who used that pernicious drug called the "devil's food." It is only since the year 1737 that the French dyers have had the right of using indigo without restriction.

Indigo exists in several varieties of plants, among which may be mentioned the *Polygonium tinctorium* and the *Isatis tinctoria*, or woad; but, as in the case of nearly all the dye-stuffs already spoken of, it is found most abundantly in plants of the leguminous order. It is extracted commercially from the genus *Indigofera*, varieties of which grow abundantly in India, Java, China, and in some of the South American States.
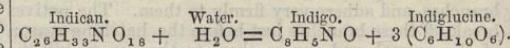
To extract the indigo which the plant contains, it is mowed when in full flower, made into bundles, and carried into large vats containing water. Fermentation ensues, which is allowed to proceed for eight or nine hours, when the liquor, which was yellow at the beginning of the operation, assumes a dark green colour, forming a blue scum on the surface. This liquor is then run off into shallow vats, where it is violently agitated with sticks, stirred by men or women, or with a dasher, which produces the same result, the conversion of the white, soluble indigo into blue insoluble indigo. A little lime-water is now added, and the whole allowed to rest. The blue indigo thus deposited is boiled with water, when a scum, composed of vegetable and animal matters, comes to the surface, and is removed. The blue paste is thrown on a filter, pressed, and placed in wooden frames, which are divided into small squares, where the indigo is allowed to dry first in the sun, and afterwards in the shade. The quality of the indigo produced depends mainly on the care bestowed on its manufacture.

Until 1855 we had no correct ideas as to the state in which the indigo existed in the *Indigofera* plants, nor of the changes which it underwent during the process of extraction. It had been stated by M. Chevreul, many years before, that white indigo was oxidised into blue. But in the above year, and subsequently, in 1857 and 1865, Dr. Schunck published a series of papers, in which he described the true nature of the chemical changes which take place in the manufacture of indigo. He operated on the *Isatis tinctoria*, or woad, which contains the same colour-giving principle as the *Indigofera* and is the only plant yielding indigo that grows freely in this country.

By these researches, he demonstrated that indigo existed in the plants, combined with a sugar, forming a glucoside, to which he gave the name *indican;* this compound, under the influence of fermentation in the manufacturing process, was unfolded into indigo and sugar. By treating the dried woad with ether or alcohol, Dr. Schunck obtained indican, and, among other processes for its extraction, gives the following simple one. He treats the pounded dried woad leaves with ether in a displacement apparatus, and distils off the greater part of the ether. The remaining green liquor is then evaporated at a moderate temperature, a little cold water added to the syrupy residue, and the insoluble chlorophyl and other matters separated by filtration. The yellow liquid thus obtained is evaporated, either spontaneously or in vacuo.
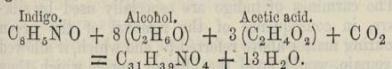
Indican is a yellow, transparent, glutinous solid. As may be seen from the above, it is soluble in alcohol, ether, and water. When boiled with caustic alkalies, it evolves ammonia, but its most remarkable and interesting property is that of yielding indigo blue when treated with strong acids. If sulphuric or muriatic acid be added to its water solution, no change whatever is perceptible for some time. But on heating to near the boiling point, the solution immediately becomes sky-blue. On boiling for a short time, the solution becomes opalescent. On continuing to boil, it acquires a purple colour; and then, provided the solution is tolerably concentrated, a copious deposit of dark purple flocks is formed. These are collected on a filter, and washed with water. By treating the washed flocks with alcohol, Dr. Schunck obtained pure indigotine, and a reddish blue substance was dissolved, called by Berzelius indigo-red, and by Schunck indirubine, which may be considered as a product of the decomposition of indican.

The colour-giving principle of the plant may be considered, like those of the dyewoads, as a glucoside, yielding by its decomposition a colourless principle, which is afterwards converted into a colour. Dr. Schunck explains by the following formula the decomposition of indican into indigo:—

$$\underset{\text{Indican.}}{C_{26}H_{33}NO_{18}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Indigo.}}{C_8H_5NO} + \underset{\text{Indiglucine.}}{3(C_6H_{10}O_6)}.$$

In 1864 he published a most valuable paper, throwing much light on the manufacture of indigo, and the management of what is called a woad vat. In it he gives the chemical actions which take place, and explains why, if the indigo manufacturer does not take the greatest care in conducting the process of fermentation, to extract the indigo from the plant, he will either get an inferior quality of indigo, or a great decrease in the yield of the product, or even in some cases entirely lose the colouring matter. He shows that these results take place when the fermentation in the vats is allowed to be either too rapid or too prolonged, in which cases not only is indican decomposed, but the *indiglucine*, or sugar, is converted into alcohol and acetic acid; and he shows that the indigo combines with this alcohol and

acetic acid, yielding a compound which does not permit the indigo it contains to be oxidised on exposure to the air. This explains the loss of indigo in its manufacture. Dr. Schunck represents the change by the foling formulæ:—

$$\underset{\text{Indigo.}}{C_8H_5NO} + 8\,\underset{\text{Alcohol.}}{(C_2H_6O)} + 3\,\underset{\text{Acetic acid.}}{(C_2H_4O_2)} + CO_2$$
$$= C_{31}H_{39}NO_4 + 13\,H_2O.$$

He produced this compound more easily by treating pure indigo blue with alcohol, to which was added an alkaline solution of protoxide of tin, until the indigo was dissolved, acetate of soda was then added, and the whole digested at a moderate temperature. The indigo blue after some time ceased to be deposited on exposure to air, having entirely disappeared, having been converted into the new compound.

Pure indigo, or indigotine, can be prepared from indican, by the process already described, or by reducing indigo to powder, placing it in a small dish on which is a cover, and applying a heat of about 300° or 400° Fahr., when beautiful prismatic needles of indigotine are sublimed, which are removed mechanically. It is insoluble in water, alcohol, or ether, or in weak acids, or alkalis, but is slightly soluble in creosote, carbolic acid, and anhydrous acetic acid, to which a very small quantity of sulphuric acid has been added. From this latter solution, the indigotine may be precipitated by the addition of water. It is the only solution of blue indigo that can be applied directly on a fabric.
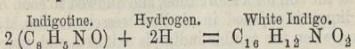
Indigotine, when heated, gives off beautiful violet vapours, having a characteristic odour. Under the action of oxidising agents, such as nitric acid, it yields three distinct products, *isatin*, $C_8H_5NO_2$; *indigotic or nitrosalicylic acid* $C_7H_3(NO_2)O_3$, and picric acid, $C_6H_3\,3(NO_2)O$. The first is formed by simple oxidation, whilst in the second and third, part of the carbon is oxidised, and hyponitric acid is substituted for part of the hydrogen. These chemical reactions lead me to call your attention to some very interesting scientific deductions, showing indigo to bear a very close relation to aniline and carbolic acid, both products derived from coal-tar. If indigotine is heated with potash in a small retort, aniline is produced, and distils over. When indigo is heated for some time with caustic potash solution of specific gravity, 1·35, it yields anthranilic acid, which may be considered as a phenyle-carbamic acid. Anthranilic acid again, being heated to 570° Fahr., gives salycilic acid, which may be considered as a compound of carbonic with carbolic acid. Lastly, indigotine, like carbolic acid, yields on treatment with excess of nitric acid, picric, or trinitrophenic acid.

These facts have produced on the minds of chemists a conviction that indigotine will one day be artificially prepared from carbolic acid, and recently MM. Emmerling and Engler have accomplished the scientific artificial production of indigotine from a compound acetone, discovered in 1857 by M. Friedel, to which these gentlemen have given the name of acetophenone. Their process consists in acting on this compound with fuming nitric acid, when two nitro-compounds are produced, one crystalline, the other syrupy. To the latter, after its evaporation to the state of a resinous mass, they add ten parts of reduced zinc and one part of soda-lime. The mixture is heated in small tubes, when a little water evaporates and a dark coloured substance sublimes, which contains indigotine in small quantities. This result is certainly a triumph of scientific chemistry, and brings us another stage nearer the commercial artificial production of a most valuable dye.

A great variety of substances, by adding one equivalent of hydrogen, convert blue indigo into white indigo, which is a colourless substance, without taste or odour, insoluble in water, but soluble in alcohol and ether, and in solutions of the alkalis and alkaline earths. On this point I may observe that, many years ago, I devised a process, by which many pounds worth of indigo were recovered from the refuse bottoms of the blue dip vats, the preparation of which I shall explain further on. I found that indigo was susceptible of forming insoluble compounds with the lime and protoxide of iron. White indigo dissolves freely in strong sulphuric acid, giving a dark purple blue liquor.

Many substances are employed commercially to convert blue indigo into the white indigo, soluble in alkalies. Thus, I may mention lime and protoxide of iron, caustic alkali and protoxide of tin, or sulphuret of tin or arsenic, and zinc and caustic alkali; also organic substances, such as grape sugar and bran, which enter easily into fermentation. The following formulæ show the difference of composition of the two indigos:—

$$2\,\underset{\text{Indigotine.}}{(C_8H_5NO)} + \underset{\text{Hydrogen.}}{2H} = \underset{\text{White Indigo.}}{C_{16}H_{12}NO_2}$$

I shall now have the pleasure of proceeding to describe some of the methods employed by chemists to determine the relative commercial value of samples of this expensive dye. The best qualities of indigo from Bengal, Java, and Guatamala, are light, have a uniform texture, and a fine coppery hue, which is increased by friction. The following analysis, made by M. Chevreul, shows the composition of a fair sample of commercial indigo:—

Indigotine	45
Matters soluble in alcohol	30
Matters soluble in ether	12
Resin soluble in hydrochloric acid	6
Mineral matters	7
	100

Commercial indigos are often adulterated with mineral matters of various kinds. This fraud is easily detected by calcining a known weight of the sample, which ought not to leave a residue of more than ten per cent. The most common adulteration, however, is the addition of starch. This can be detected by boiling some of the pulverised indigo with a weak solution of hydrochloric acid. The insoluble starch is thus converted into soluble dextrine, which yields a beautiful purple colour with iodine.

There are several processes employed to determine the amount of indigotine in commercial indigos. I shall here only give the outline of three. The first consists in dissolving one gramme of the dry pulverised indigo in twelve grammes of concentrated sulphuric acid, and heating the whole at a temperature not exceeding 120° Fahr., when the indigo combines with the sulphuric acid, and becomes perfectly soluble in water. It is then diluted with water, so that the whole occupies one litre. The operation is repeated with one gramme of pure indigotine, which serves as a standard of comparison. A solution of bleaching powder, or bichromate of potash—the first proposed by M. Chevreul, the latter by Dr. Penny—is prepared of such a strength that one hundred volumes of the solution will completely destroy the whole of the colour produced by the gramme of indigotine. Part of the same liquor is then applied to the solution of the commercial indigo, and the number of volumes required to destroy the colour represents the per-centage of indigo. Thus, if 60 divisions are required, it is assumed that there is 60 per cent., if 70 divisions, 70 per cent. This method of estimating the indigotine is not to be relied on, as it always gives a much higher per-centage of colour-giving principle than exists in the indigo, owing to the hypochlorous acid of the bleaching powder, and the chromic acid of the bichromate not only decomposing the indigotine, but acting on several colouring matters which are included in the portion soluble in alcohol in M. Chevreul's analysis.

The second process gives better results; it is due to Professor Fritzsche, and consists in introducing one part of indigo, finely pulverised, and one part of grape sugar,

into forty-eight or fifty parts of boiling alcohol, to which is added two parts of a concentrated solution of caustic soda. The whole is put into a bottle exactly large enough to hold it, and left to cool. By exposing the colourless liquid to the atmosphere, the reduced indigo which is in solution absorbs oxygen, and the indigotine is precipitated under the form of beautiful prismatic crystals.

The third process, devised by myself, I have found to give satisfactory results. It consists in introducing into a flask one part of finely pulverised indigo, two parts of green copperas, and two hundred parts of water containing ten per cent. of caustic soda. The whole is kept at the boil for a short time, and allowed to cool. The clear liquor is exposed in shallow vessels to the atmosphere, when the soluble indigo is oxidised, and precipitates as pure indigotine. The residue in the flask is submitted to the treatment three times. The whole of the indigotine thus obtained is collected on a filter, dried, and weighed.

A commercial process, founded on the above method, is carried on by Messrs. Haas and Co., who sell indigo so purified under the name of refined indigo. An inferior quality is also prepared by heating indigo, at a moderate temperature, with weak muriatic acid, which dissolves lime and other mineral matters, as well as any starch it may contain; it is slightly washed and boiled with weak caustic soda, to dissolve the chlorophyl and other resinous impurities.

I shall now call your attention to three commercial preparations of indigo, obtained by the action of sulphuric acid on it. The first is called *sulpho-purpuric acid* or *phenicine*, which is made by adding one part of indigo to four parts of highly concentrated sulphuric acid, heating for a short time, varying from half an hour to an hour, or until a small quantity of it mixed with a large quantity of water gives a deep purple colour. Great care must be bestowed on this part of the operation, so as to avoid the formation of a compound, to which I shall have again to call your attention, *sulpho-indigotic acid*. The acid mass produced is thrown into about 40 or 50 parts of water, when a beautiful purple precipitate is produced, which is collected on a filter, and slightly washed with weak muriatic acid. To dye wool with this sulpho-purpuric acid it is necessary to add to the bath a little muriatic acid, when it yields to the wool a fine dark purple-blue, that can be converted into various shades of purple by passing the wool so dyed in a bath containing a small quantity of carbonate or acetate of soda, which removes a small quantity of sulpho-indigotic acid that may be present, and gives rise to *sulpho-purpurate of soda*, which is a faster dye than the acid itself.

Sulpho-indigotic Acid is manufactured by dissolving one part of indigo in ten or twelve parts of concentrated sulphuric acid, and heating the whole at a temperature of 120° F. very carefully for some hours. The operation is completed when a small quantity dissolves entirely in cold water.

The acids above described, when obtained perfectly pure, have the following formulæ:—Sulpho-purpuric acid, $C_{16} H_{10} N_2 O_2, S O_3$; sulpho-indigotic acid, $C_8 H_5 N O, S O_3$.

Berzelius admits a third compound, called *hypo-sulpho-indigotic acid*. These acids are transformed into neutral salts of soda, and sold under the names of neutral paste and carmine of indigo. They are prepared by neutralising the sulpho-acids with carbonate of soda, and the paste so formed is thrown on a woollen filter to remove the sulphate of soda which it contains, as well as a green colouring matter, which is doubtless modified chlorophyl. The paste is then washed with a solution of chloride of sodium. It is a curious fact that carmines of indigo, which are perfectly soluble in pure water, are altogether insoluble in water containing either sulphate of soda or chloride of sodium.

Whilst speaking of the sulpho-indigotates, it may be useful to notice that the sulpho-indigotates of potash and soda are soluble in 100 to 150 parts of water, the sulpho-indigotates of lime, magnesia, and alumina are freely soluble, whilst those of baryta and lead are insoluble.

The carmines of indigo are especially used by silk-dyers, in consequence of the removal of the green colouring matter above referred to, and which, if allowed to remain, would spoil the blue or purple which they wish to obtain. The method practically adopted to ascertain if the sample has been well washed, consists in rubbing a small quantity of it on a piece of glazed paper, which, when the colour dries, gives a colour varying from a pale blue to a rich copper purple, according to the mode of manufacture; and if any green colouring matter is left in, it shows itself as a green ring round the blue circle.

The following may be taken as the composition of a sample of carmine of indigo of fair quality:—

Water	85
Indigo	10·2
Saline residue	4·8
	100·0

The sulpho-indigotic acids are especially used by woollen-dyers, who add to the dye-beck a little alum and cream of tartar, which helps the fixing of the indigo on the wool. The green colouring matter is in this case not objectionable, having no affinity for the fibre of wool.

The carmines of indigo, as well as the sulpho-acids, are easily decolourised by reducing agents, such as hydrogen and sulphuretted hydrogen, but they gradually reassume their original colour when exposed to the atmosphere, through the absorption of oxygen.

The above compounds, not being suitable for dyeing cotton, and not giving colours on silk and wool that may be considered fast, I shall now proceed to describe a few of the methods followed to obtain fast indigo blues. They are all based on the principle of the reduction of blue indigo into white indigo. The latter compound is held in solution by an alkali, which enables the dyer or printer to introduce it into the fibre of the fabric, where, on exposure to the atmosphere, the alkali combines with carbonic acid, and the white indigo thus liberated absorbs oxygen, and becomes insoluble blue indigo. The principal class of goods to which this chemical reaction is applied is to the vegetable fibres, linen, and especially cotton. As far as dyeing is concerned, the processes can be classed under two heads, hot and cold. The hot process is principally applied to wool, the cold to vegetable fibres, especially cotton.

The oldest and still most generally employed method of preparing cold vats consists of putting into a vat containing about two thousand gallons of water, sixty pounds of indigo, very finely powdered, one hundred and eighty pounds of slacked lime, and one hundred and twenty pounds of sulphate of protoxide of iron or green vitrol (free from any trace of copper salt), the two latter substances being added from time to time. The greater part of the lime used unites with the sulphuric acid of the iron salt, to produce sulphate of lime or gypsum, and the liberated protoxide of iron removes the oxygen from the indigo, becoming converted into saline oxide, whilst the reduced indigo dissolves in the excess of lime employed.

Messrs. R. Schloesser and Co., of Manchester, have introduced within the last year or two a marked improvement in the preparation of cold vats, which removes the great objections of the bulky precipitate of sulphate of lime, the formation of an oxide of iron, and the loss of indigo by its combination with the oxide of iron referred to in the previous part of the lecture. The bath remaining much more fluid, the pieces are less apt to be spotted, and a better class of work is produced. To carry out their process, they add to the ordinary two thousand gallon vat twenty pounds of ground indigo,

thirty pounds of iron borings, thirty pounds of their remarkable powdered zinc, and thirty-five pounds of quick lime; the whole is stirred up from time to time for twenty-four hours, when it is ready for use. If the bath is not considered sufficiently strong, a little more lime and zinc are introduced.

The chemical theory of the process is, that the zinc, under the influence of the lime, decomposes water, combining with its oxygen, and the hydrogen thus liberated, removes oxygen from the indigo, which then dissolves in the lime.

To dye cotton yarn in the above vats, it is simply necessary to dip it for a few minutes in the dye bath, and expose it to the atmosphere, when the green hue it has acquired passes rapidly into blue. This operation is repeated until the yarn has attained the required depth of shade, when it is passed into weak vitriol, washed, and is ready for market.

To dye calicos, the pieces are hooked on frames, passed through a bath of weak milk of lime, and then dipped into the reduced indigo vat. After fifteen minutes, the frame is taken out and the cloth exposed to the air for about the same length of time. It is again dipped, the process being repeated until the required depth of tint is attained. It is then passed through weak vitriol, and washed. The cold vats are especially used when it is wished to obtain white and yellow designs on a blue ground; but when the object in view is to produce a self-colour, a more rapid process is adopted. This consists in passing the pieces through a dye-beck, then through an acid liquor, and lastly in water, by means of rollers fixed in the vat. The bath is composed of lime, sulphate of iron, and indigo, but is kept hot, instead of cold as in the former case.

There is still another process, which is now used to a limited extent only, but was at one time very extensively employed. It produces on the cloth a pale blue, which has a great similarity of tint to that seen on the china porcelain, from which it derives its name of china-blue. To produce it the pieces are printed with a mixture containing very finely-powdered indigo, and a little acetate of iron, and are made to pass through six successive vats. The first two contain lime, the third sulphate of iron, the fourth a solution of caustic soda, the fifth a dilute solution of sulphuric acid, and the sixth water. When the design has acquired the required depth of blue, the pieces are washed, passed once more through weak sulphuric acid, and again washed. The chemical reactions are exactly similar to those in the cold vat process.

For dying wool, a modification of the old woad vat is employed. The use of woad being now almost entirely discontinued, I shall merely call your attention to the process in which indigo has been substituted for woad. It bears the name of Indian vat, doubtless from the process having been practiced in India and imported from thence. It is as follows:—Eight pounds of powdered indigo is added to a bath containing $3\frac{1}{2}$ pounds of bran, $3\frac{1}{2}$ pounds of madder, and 12 pounds of potash, which is maintained for several hours at a temperature of 200° Fahr. It is then allowed to cool to 100° Fahr., when fermentation ensues. After about forty-eight hours, the indigo is rendered soluble, being reduced, by the decomposition of the sugar and other products contained in the bran and the madder-root during the process of fermentation. The bath should have a greenish yellow appearance, having a frothy scum of a blue coppery hue.

Of late years, improvements have been made in this class of vats, by which the expense of using madder is avoided. They are now prepared by adding to water, at a temperature of 200° Fahr., twenty buckets of bran, twenty-six pounds of soda crystals, twelve pounds of indigo, and five pounds of slacked lime. After five hours, the bath is allowed to cool to 100° Fahr., when fermentation ensues, and the indigo is dissolved in the alkali. The management of these vats require great experience and care, for if the fermentation is too slow the indigo is not properly reduced, whilst if too active large quantities of indigo

may be lost. The researches of Dr. Schunck, already referred to, not only show the method of avoiding this loss, but explain why it occurs. The remarks which I made as to the causes of failure in the manufacture of indigo are applicable here, namely, that if the fermentation becomes alcoholic and acetic, the non-oxidisable indigo compounds described by Dr. Schunck are generated.

I cannot leave the subject of indigo without bringing before you a most curious source of its production, namely, the human body. Medical men had observed from time to time that urine, secreted under certain pathological conditions, became brown, and sometimes even blue, when exposed to the atmosphere. The late Dr. Hassel discovered that in some instances the colouring matter was indigo, but here, again, we are indebted to Dr. Schunck for much information on the subject. In three papers presented to the Royal Society, he has proved that urine, in cases similar to those examined by Dr. Hassel, contained the glucoside of indigo, or indican. He also observed that indican was a very frequent constituent of urine secreted by persons in a healthy state, and, in fact, that it is produced generally when persons do not take sufficient exercise, and he has on several occasions succeeded in producing it by taking in his food a rather large excess of sugar.

Orchil, Cudbear, Litmus.—I shall now call your attention to a colour which was discovered in 1300, by an Italian named Federigo, who, during his travels in the East, observed the tinctorial powers of a certain class of weeds called *lichens*, and he introduced the colour into Florence under the name of *orchil*. By this discovery he and his family made a very large fortune.

Lichens are small plants which live either in the stems or leaves of trees, or on rocks, or damp soils. To this class belongs all the vegetation found in the Arctic circle, but the species growing there are not employed to produce the colouring matter orchil, the varieties used for this purpose being found in warmer, and especially in tropical climates. These latter can be divided into two classes; the first and most abundant, which grow on rocks near the sea-side, includes the species *Roccella tinctoria* and *Roccella fuciformia*. They are obtained from the Canary Islands, Cape Vere, and Sardinia, but principally from Madagascar, Zanzibar, Angola, and South America. The second class grows inland, and includes the species *Variolaria orcina*, found especially in the Pyrénées.

Lichens do not contain any colouring matter already formed, but contain colourless acids, which, under the influence of ammonia and the oxygen of the atmosphere, give rise to the orchil. As the lichens imported into this country vary considerably in the amount of orchil which they yield, Dr. Stenhouse has rendered a great service to the manufacturers in furnishing them with a simple and accurate process of ascertaining their commercial value. The following is an outline of his method:— One hundred grains of the lichen are macerated with a dilute solution of caustic soda, two treatments being sufficient to extract the whole of the colouring matter. A solution of hypochlorite of sodium of known strength is added to the soda solution from a graduated alkalimeter; the moment the bleaching liquor comes in contact with the soda solution of the lichen a blood red colour is produced, which disappears in a minute or two, and the liquid has only a deep yellow colour. A new quantity of bleaching liquid should then be poured into the soda solution, and the mixture carefully stirred. The operation should be repeated as long as the addition of the hypochlorite of sodium causes the production of the red colour, for this shows that the soda solution still contains unoxidised colouring principle. Towards the end of the process the bleaching solution should be added by only a few drops at a time, the mixture being carefully stirred between each addition. By noting how many measures of the bleaching liquor have been required to destroy the colouring matter in solution,

the amount of colouring principle contained in the lichen may be determined.

The manufacturers of orchil, are also indebted to Dr. Stenhouse for a process of obtaining the orchil, which, besides simplifying the operations required, gives brighter colours and extracts than could be produced before the publication of his method, in 1848. Of this you will easily judge when I tell you that the process carried on for centuries, consisted in breaking up the weeds in water, to which putrid urine, lime, and carbonate of soda were added from time to time. After two or three months' exposure to the air, the colourless principles of the lichen became transformed into the colouring matter orchil. As the science of chemistry progressed, and cheap means of producing ammonia were devised, this compound was substituted for the urine. Dr. Stenhouse's process consists in exhausting the lichens, by macerating them with milk of lime, squeezing the liquor off, and after having repeated this treatment two or three times, he adds an acid to the liquors, when a white gelatinous precipitate is produced, which, when collected and placed in contact with ammonia, gives rise to orchil.

You are doubtless aware that the beautiful purple and mauve colours obtained on silk and wool from orchil are extremely fugitive, losing their brilliancy on exposure to the light or to the influence of weak acids, such as sulphurous, which is so abundantly produced in our manufacturing districts. M. Marnas, of Lyons, succeeded in the year 1856, in making orchil colours which gave fast purples and mauves.

Before describing this valuable discovery, allow me to state that it had a most important bearing on the marked progress which the art of calico-printing has made since the date above mentioned. Until that time, neither dyers nor calico printers would use expensive dyes, but since then, they have paid as much as £40 or £50 per pound for the solid dyestuff, although these enormous prices have been apparently decreased by the colours being sold in the state of paste or solution.
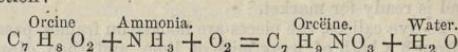
The demand for a fast purple in this country was so great, consequent on the introduction of the fast purples and mauves on the Continent by M. Marnas, that attention was directed to the preparation of these colours. Mr. Perkin had obtained from aniline a fine purple colour, as fast as the orchil colours, and M. Bechamp discovering about this time a method of producing aniline artificially from benzine, Mr. Perkin was enabled to manufacture his colour commercially. This may be considered as the first successful step towards the introduction of the splendid and varied coal-tar colours which are now so universally admired.

Returning from this digression, let us now enter on a description of the process of M. Marnas. He treated the lichens, as suggested by Dr. Stenhouse, with milk of lime, filtered the lime liquor off, precipitated the colour-giving principle from it with hydrochloric acid, and gathered the precipitate on a filter. This precipitate was well washed, dissolved in caustic ammonia, and the ammoniacal liquor kept at a temperature of 153° to 160° for twenty to twenty-five 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. These were separated from the liquid by the addition of chloride of calcium, which caused a fine purple-lake to be deposited. This, after being washed and dried, was sold under the name of French purple.

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 through in the filtrate. This liquor is added to a slightly ammoniacal liquid in the dye-beck; all that is now necessary is to dip the silk or wool in the beck, when they will become dyed with magnificent purple or mauve.

To dye cotton, it is necessary to mordant it with albumen, or prepare it as for Turkey red, before putting it in the bath.
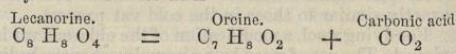
Robiquet was the first chemist to isolate a colourless principle from lichens susceptible of assuming a fine purple hue when brought in contact with ammonia and oxygen. This principle he named *orcine*. He obtained it by treating the *Variolaria orcina* by strong alcohol. This solution, on being allowed to cool, gives crystals, which, on being dissolved in water and allowed to crystallise, assume the form of large well-defined crystals of hydrate of orcine. By crystallisation from ether anhydrous orcine can be obtained. Orcine gives a fine, dark red colour with perchloride of iron; but its most remarkable property is its transformation into *orcëine*, which Robiquet shows to be due to the following reaction:—

$$\underset{\text{Orcine}}{C_7\,H_8\,O_2} + \underset{\text{Ammonia.}}{N\,H_3} + O_2 = \underset{\text{Orcëine.}}{C_7\,H_9\,N\,O_3} + \underset{\text{Water.}}{H_2\,O}$$

Orcëine presents itself under the form of a brown powder, slightly soluble in cold water, to which it gives a red colour. It is soluble in alcohol, but insoluble in ether. It is soluble in alkalis and ammonia, to which it communicates a magnificent violet colour. It exists in commercial orchil under the form of orcëinate of ammonia.
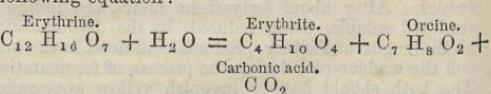
Time will not permit me to describe the researches of Heeran and Sir R. Kane. I must therefore confine myself principally to a short description of those of Dr. Stenhouse and Dr. Schunck.

The chief merit of Dr. Schunck consists in having pointed out the connection which exists between the orcine of Robiquet, and the *erythrine* and *pseudo-erythrine* of Heeran, and in showing that orcine is the sole immediate colour-producing principle of the series. This he proved by his researches published in 1842, in which he treated the dried and powdered variolaria orcina by ether. On evaporating this solution, there remained a residue, from which he isolated a substance which he called *lecanorine* or *lecanoric acid*. This compound crystallises in white needles, and gives a red colour with bleaching powder, and a dark purple with perchloride of iron. It yields a similar colour when dissolved in ammonia and exposed to the atmosphere. Its most interesting property is its conversion into orcine and carbonic acid, when boiled with an aqueous solution of baryta. The reaction is—

$$\underset{\text{Lecanorine.}}{C_8\,H_8\,O_4} = \underset{\text{Orcine.}}{C_7\,H_8\,O_2} + \underset{\text{Carbonic acid}}{C\,O_2}$$

He found also that on boiling lecanorine with alcohol it formed an ether, which proved to be identical with the pseudoerythrine of Heeran.

Dr. Stenhouse has succeeded in extracting the important compounds to which he has given the names of *erythrite* and *orsellic acids*. The first-mentioned body is a product of the decomposition of erythrine under the influence of lime-water. The erythrine splits up into carbonic acid, orcine, and erythrite, according to the following equation :—

$$\underset{\text{Erythrine.}}{C_{12}\,H_{16}\,O_7} + H_2\,O = \underset{\text{Erythrite.}}{C_4\,H_{10}\,O_4} + \underset{\text{Orcine.}}{C_7\,H_8\,O_2} + \underset{\text{Carbonic acid.}}{C\,O_2}$$

The orsellic acids were obtained, one from the South American weed, the other from the South African. The first appears to be identical in composition with lecanorine, and is capable of splitting up under the influence of baryta or lime into carbonic acid and orcine. The one from the latter appears to be composed of lecanoric acid and a substance called roccellinine. According to Schutzenberger, lecanoric acid may be made to undergo a decomposition into orselic acid, or may be further converted into orcine.

The employment of orchil is at the present day comparatively limited, but it is still used for producing
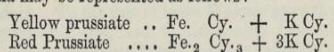
browns, maroons, and other dark shades, in conjunction with other dye-stuffs. Its chief use is to top cheap indigo blues on woollen goods; this is effected by lightly dying the fabric with indigo (an expensive dye) and then passing it through a bath of orchil, which gives to the cloth a rich purple hue, similar in appearance to one dyed wholly with indigo.

Cudbear is a special preparation of orchil, first manufactured by Dr. Cuthbert Gordon, from whom it derives its name.
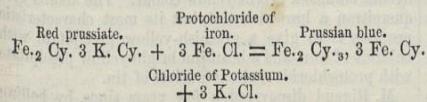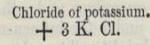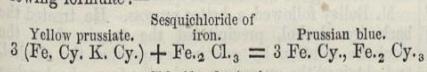
Litmus is obtained from the same lichens as those employed for producing orchil, only lime and carbonate of potash are added to the ground weed and urine; in fact the process is very similar to that used in former times to produce orchil. After three or four weeks, a blue colour is fully developed, when it is mixed with sulphate of lime or chalk, dried, and is ready for market. The chief employment of litmus is to communicate a peculiar tint to the cheese made in Holland.

Prussian Blue.—I shall now have the pleasure of drawing your attention to one of the finest, brightest, and most permanent colours known. It was discovered accidentally in 1710, by a colour manufacturer named Diesbach, of Berlin, from which it derived its name. The process by which it was produced was kept a comparative secret until 1724, when Dr. Woodward showed how the colour had become a very profitable affair, and described a process by which it could be obtained. The process has in time undergone many improvements; but I shall here confine myself to a description of it as now carried out. I shall be obliged here to enter slightly into theoretical chemistry.

Prussian blue is a combination of iron with *cyanogen*, a compound of carbon and nitrogen. There are two well-defined cyanides of iron corresponding to the two oxides, the *proto-cyanide*, Fe. Cy. and the *sesquicyanide*, Fe$_2$. Cy$_3$. These two cyanides, combining together in different proportions, give rise to the various shades of Prussian blue found in commerce. But, strange to say, you cannot produce either of these compounds or Prussian blue by the direct combination of cyanogen with iron. Cyanogen must be first united with potassium, giving rise to cyanide of potassium, under the influence of which salt the iron combines with cyanogen, and the cyanide of iron thus formed in its turn combines with the cyanide of potassium, forming a double cyanide. There are two double cyanides of potassium and iron; the first, called ferro-cyanide of potassium, or yellow prussiate of potash; the second, ferri-cyanide, or red prussiate of potash. The formula may be represented as follows :—

$$\text{Yellow prussiate .. Fe. Cy.} + \text{K Cy.}$$
$$\text{Red Prussiate .... Fe}_2 \text{ Cy}_3 + \text{3K Cy.}$$

To produce Prussian blue from these salts, it is necessary to replace the potassium by iron. This is effected by adding a persalt of iron to the yellow prussiate or to the red prussiate, a proto-salt of iron. The iron of the iron salt replaces the potassium of the double salts, and double cyanides of iron are produced, as seen by the following formulæ :—

Sesquichloride of
Yellow prussiate.   iron.   Prussian blue.
$$3\,(\text{Fe, Cy. K. Cy.}) + \text{Fe}_2 \text{ Cl}_3 = 3\,\text{Fe. Cy., Fe}_2 \text{ Cy}_3$$
Chloride of potassium.
$$+ \text{ 3 K. Cl.}$$

Protochloride of
Red prussiate.   iron.   Prussian blue.
$$\text{Fe}_2 \text{ Cy. 3 K. Cy.} + \text{ 3 Fe. Cl.} = \text{Fe}_2 \text{ Cy}_3, \text{3 Fe. Cy.}$$
Chloride of Potassium.
$$+ \text{ 3 K. Cl.}$$

That this is the case can be easily demonstrated, for if you mix together a solution of persalt of iron and one of red prussiate, which contains only percyanide of iron, no Prussian blue is formed. Again, if you mix yellow prussiate of potash with protochloride of iron, you get no Prussian blue, because, in the first case, you have no protocyanide of iron present, and, in the second, you have no percyanide.

Simple as the production of Prussian blue appears, it requires much practice to prepare it with certainty as a pigment where a given shade of blue is required. It is seldom found pure in commerce, being generally mixed with starch, chalk, or gypsum. Sometimes they are added with a view to deception, sometimes in order to produce a lighter shade of colour. The testing of a Prussian blue by chemical means is not, therefore, a true criterion of its quality. The method usually employed consists in grinding in oil equal weights of a Prussian blue of known value and of the one to be tested, white lead is added to each, and the intensity of the colours compared.

The best quality of Prussian blue is obtained by mixing a dilute solution of red prussiate of potash with proto-salt of iron; the second quality is made by mixing yellow prussiate of potash with pernitrate of iron, and is called *Turnbull's blue*. Cheaper qualities are made by mixing solutions of yellow prussiate and proto-sulphate of iron (green copperas), which produces a pale-blue precipitate. This is transformed into Prussian blue by the addition of bleaching powder, which oxidises part of the iron, and transforms the protocyanide into percyanide. For still lower qualities, alum is mixed with the iron solution previously to the prussiate being added. Alumina is by this means mixed with the blue.

Prussian blue was first obtained on silk fabrics in 1811, by a professor of chemistry at Lyons, named Raymond, in consequence of the high premium offered by the First Napoleon for the production of a fast blue, as indigo could not at that time be imported into France. His process, with slight modifications, is followed at the present day, although the colour is not much used, owing to the introduction of the aniline blues. It consists in dipping the silk, for several hours, in a salt of peroxide of iron, when the oxide of iron becomes fixed in the silk, which is washed and dipped in a slightly acid solution of yellow prussiate of potash. Prussian blue is thus produced on the silk, which only requires washing to be ready for market. The only improvement made in this class of dying has been the addition of a persalt of tin to the iron-salt.

The production of Prussian blue on cotton or woollen fibres is effected by a curious chemical reaction. At a temperature of 212° Fahr., all acids, even the organic, such as oxalic, citric, and tartaric, as well as the acid sulphates, possess the property of decomposing the two prussiates. The potassium of the cyanide combines with oxygen of the water, and with the organic acid. The cyanogen thus liberated unites with the hydrogen of the water, forming prussic acid. The cyanide of iron liberated unites with the fibre of the cloth, and on the latter being passed into a weak solution of bichromate of potash or bleaching powder, or if it is left exposed to the air, part of the proto-cyanide of iron is converted into sesquicyanide, and Prussian blue is produced. As salts of tin greatly facilitate the fixing of the prussiate on the cloth, chloride of tin is now generally mixed with the prussiate of potash. In this case prussiate of tin is produced. To this mixture tartaric or oxalic acid is added; it is then properly thickened and printed on the calico. When the design is dry, the fabric is submitted to the action of steam, and the blue is produced on the fabric. It then only requires to be passed through a bath of bichromate of potash, to develop the full depth of the shade.

Ultramarine Blue is a most valuable pigment, both on account of its cheapness, and the brilliancy of its colour. It is used extensively in many branches of trade—by the calico printer in pigment printing, by the paper stainer and manufacturer, the typographic and lithographic printer, by the match manufacturer, the sugar refiner, and by the house decorator. The value of the pigment depends on the fineness of the powder, and the brilliancy of its hue.

The greatest care and much experience are required in every stage of the manufacture, in purifying the substances employed, in mixing, in heating at the proper temperature, and in grinding, washing, and drying the manufactured mass. Fourteen distinct operations are required to produce it, and it would take too much time at this late hour to enter into the details of these processes. I will therefore only attempt to give you a very rough outline of the principal points of the manufacture.

The proportion of materials used, may be as follows :—

White china, clay, or kaolin	50	parts.
Sulphate of soda	19	,,
Sulphur	25	,,
Charcoal	12	,,
Carbonate of soda	28	,,
	134	

These substances are most intimately mixed together and introduced into an earthenware crucible, which is carefully closed and heated at a temperature of about 500°F. for twelve hours. The temperature is then gradually raised till it reaches a white heat at the end of 48 hours; the fire is then removed, and the crucible allowed to cool gradually in the furnace. The mass, as taken out of the crucible, is of a beautiful bright green colour. It is ground, washed, and dried, and then calcined in in an open furnace, to oxidise it; but as the slightest excess of oxidation spoils the colour, the workman from time to time adds a small amount of sulphur to the mass,

by this means controlling the oxidation. The green mass gradually becomes blue, and is washed and dried, when it is ready for market.

The colouring matter of ultramarine is not well known. It is supposed to be a peculiar sulphite or hyposulphite of soda. The solid matter itself is a double silicate of soda and alumina. What is certainly worth notice is that, although we are ignorant of the true colouring matter of this pigment, we find its composition to be almost identical with that of the natural *Lapis lazuli*, which, although very costly, was employed by printers for many centuries. The following analyses will show the similarity of composition :—

	Lapis lazuli.		Ultramarine.
Silica	45·40	....	46·60
Alumina	31·67	....	23·30
Soda	9·09	....	21·46
Potash	*nil*	....	1·75
Iron	0·52	....	1,06
Lime	3·52	....	0·02
Sulphuric acid	5·89	....	3·08
Sulphur	0·95	....	1·68
Chlorine	0·42	....	trace.
Water	0·12	....	*nil*
Loss	2·42	....	1·05
	100·00		100·00

Artificial ultramarine was discovered by a French chemist and druggist, named Guimet, who kept the process of its manufacture secret for many years.

LECTURE IV.—Delivered Tuesday, February 28th, 1871.

QUERCITRON, FUSTIC, PERSIAN BERRIES, WELD, ALOES, TURMERIC, ANNATTO, ILIXANTHINE, LO-KAO, TANNIN MATTERS—GALL NUTS, SUMACH, DIVI-DIVI, MYROBALANS, CATECHU.

I shall have the pleasure of devoting the first part of this lecture to some of the most useful and important yellow substances used by dyers and calico-printers, and to one or two other colouring matters which, although scarcely commercially important, are interesting from a scientific point of view.

Among the most valuable of these bodies is *quercitron*, the bark (from which the epidermis has been removed) of a particular species of oak, called the *Quercus nigra* or *Quercus tinctoria*. This tree is indigenous to the United States of America, and is especially found in the forests of Pennsylvania, Georgia, and in North and South Carolina. A chemist, of the name of Bancroft, first introduced it to the English dyers in the year 1775. The most esteemed qualities are those imported from Philadelphia, New York, and Baltimore. The bark, after being removed from the tree, is dried, and ground between mill-stones. The value of a sample bears a direct ratio to the fineness of the powder, for the woody fibre of the bark, which contains only a small quantity of colouring principle, is not easily reduced to a fine powder.
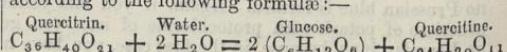
M. Chevreul was the first chemist who examined this dye, and he found it to contain a peculiar tannin, which has since received the name of *quercitannic acid*, and a

yellow colouring principle, to which he gave the name of *quercitrin*, but which has since received the name of *quercitric acid* from M. Bolley.

M. Chevreul, by boiling quercitron bark in water, and allowing the aqueous solution to stand, obtained fine, laminated crystals, which were gradually deposited, and to which he gave the name of quercitrin.

M. Bolley followed a better process. He treated the bark by alcohol, precipitated the tannin from the alcoholic solution by gelatine, evaporated the alcohol, and obtained the quercitron under the form of colourless crystals. These, under the influence of air or oxidising agents, assume a bright yellow colour. The alkalis give quercitron a brownish tint, but its most characteristic property is to give a greenish-yellow precipitate with chloride of iron, and a beautiful bright yellow precipitate with protochloride and oxymuriate of tin.

M. Rigaud discovered, a few years since, by boiling quercitron with water containing 10 per cent. of sulphuric acid, that it is a glucoside, which decomposes under the influence of the acid into glucose and quercitrin according to the following formulæ :—

$$\underset{\text{Quercitrin.}}{C_{36}H_{40}O_{21}} + \underset{\text{Water.}}{2\,H_2O} = 2\,(\underset{\text{Glucose.}}{C_6H_{12}O_6}) + \underset{\text{Quercitine.}}{C_{24}H_{20}O_{11}}$$

Quercitrin is a crystalline powder, of a bright lemon colour, and of a much richer hue than quercitron. It has no taste, is insoluble in cold water, and only slightly soluble in hot, but is freely soluble in alcohol. It is soluble in alkalis, to which it communicates an orange-yellow hue. Its alcoholic solution gives orange precipitates with the salts of lime, baryta, and lead. It assumes an orange colour with perchloride of iron.

Although quercitron bark gives a fine yellow colour on woollen goods, when mordanted with salts of tin, to which has been added alum or cream of tartar, still its employment has greatly decreased of late years, owing to its colour assuming a reddish hue when exposed to the atmosphere.

Within the last twenty years, a preparation from it has been imported into this country from America, under the name of *flavine*, which in reality may be considered as commercial quercetine. It is now manufactured in England by two different processes. The first consists in boiling half a ton of quercitron bark with sixty-three pounds of soda crystals, in about 2,000 gallons of water; after boiling for about a quarter of an hour, 250 pounds of concentrated oil of vitriol are added. The whole is then maintained at the boil for two hours, when it is run off on to woollen filters, washed until free from acid, pressed, and dried, and is ready for market. The second process, which I consider the better one, consists in boiling for two hours one hundred parts of quercitron bark with three hundred of water and fifteen of oil of vitrol, and then washing, pressing, and drying, as in the first process. One hundred parts of quercitron bark give eighty-five of flavine, which have a dyeing power equal to 250 parts of quercitron.

Flavine is not much employed in calico printing as a yellow dye, its principal use being to communicate a brown and orange hue to madder reds.

The best mode of estimating the value of a sample of quercitron bark or flavine is to dye some mordanted cloth in the same way as in testing the value of a madder or garancine.

We shall now pass to the study of another colouring matter, called *old fustic*. The tree which supplies it is called *morus tinctoria*, and grows in the Brazils, Mexico, and in Jamaica, Cuba, and other islands of the West Indies. It arrives in this country in logs of various sizes. Dyers prefer those which are dense, are not worm-eaten, and which are of a fine orange yellow tint in the inside.

In this case, again, my master, M. Chevreul, was the first to isolate the two colouring matters which the wood contained. To the first of these Wagner gave the name of *morintannic acid*, and to the second that of *moric acid*. To extract these, rasped fustic is boiled twice with water and the solution concentrated to the state of a syrup, when after a few days a crystalline deposit takes place, which is separated, washed rapidly with cold water, and pressed. To separate the two colour-giving principles, the pressed mass is treated with boiling water, which leaves the moric acid as an insoluble mass, while the morintannic acid is dissolved. The moric acid is treated with weak hydrochloric acid, to remove some lime salts; it is then dissolved in alcohol, from which it crystallises in the form of yellow needles. To obtain the morintannic acid which was dissolved, the solution is concentrated, when the colouring matter crystallises out, and only requires recrystallising once or twice from acidulated water to give it almost pure. It forms yellow crystals, soluble in alcohol, which have the formula $C_{13}H_{10}O_6$. It gives a greenish black precipitate, with sulphate of protoxide of iron, and, with salts of lead, a yellow precipitate, soluble in acetic acid. It is decomposed by concentrated alkalis, and when boiled with zinc and sulphuric acid, the solution assumes a very bright red colour, due to the transformation of morintannic acid into two most interesting substances, *phloroglucine* and *machromine*.

Moric acid, though insoluble in water, is freely soluble in alcohol and ether, but is insoluble in bisulphuret of carbon. It is soluble in alkalis, to which it gives a yellow colour, and from this solution it is reprecipitated by the addition of an acid. Perchloride of iron communicates to its alcoholic solution an olive green shade. It gives yellow precipitates with salts of zinc, tin, lead, and alumina, and a dark green precipitate with copper. It has the formula $C_{12}H_8O_5$.

Old fustic is especially employed for dyeing wools in yellow or olive green shades. They are mordanted with a salt of alumina for yellow, or with a salt of iron for green. By the employment of salts of copper and other mordants a variety of shades can be obtained. It is much used by dyers, but only to a limited extent by calico printers.

Young fustic belongs to the same genus as sumach, of which I shall speak further on, and its botanical name is *Rhus cotinus*. It grows in the West Indies, and in France and the southern parts of Europe. It is found in commerce in the form of small logs and crooked branches. Young fustic contains a tannin matter and three colour-giving principles, a red, a brown, and a yellow. The yellow colouring matter, when isolated and crystallised, bears the name of *fustine*. It is soluble in water, alcohol, and ether. Alkalis communicate to it a fine orange hue. It rapidly oxidises when exposed to the atmosphere, assuming an orange colour. A decoction of the wood is affected by the alkalis and air in the same manner as fustine. It gives a bright orange precipitate with lime and baryta waters, and a similar coloured precipitate with chloride of tin. Persulphate of iron yields with it an olive green precipitate. Young fustic dyes wool mordanted with salts of alumina a fine orange colour, but it is easily affected by light; its chief employment is in conjunction with cochineal, to the red colour of which it imparts a brilliant orange hue. It is much used in Turkey and the Tyrol by tanners, to impart to their leather an orange yellow colour.

Persian berries, which are extensively employed by woollen and mixed fabric dyers, calico printers, paper-stainers, and leather dressers, are the berries or fruit of a genus of plants called *Nerprun*, which grows freely in France, Spain, Turkey, Persia, &c. Generally speaking, the berries are gathered before they are quite ripe, which is the reason why the berries, which are the size of a small pea, have a yellowish green shrivelled appearance. The berries only give good results when recently gathered; after one or two years they lose a great deal of their value, not yielding to the dyer such brilliant hues. The yellower they are, the less price they command in the market. They bear among the dealers the names of the countries from which they are imported; thus there are Avignon berries, Spanish berries, Turkish berries, and Persian berries. The latter are the best, and are obtained from the *Rhamnus amygdalinus*. Among dyers and calico printers all the varieties are called Persian berries.
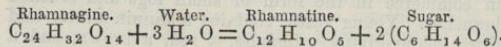
The yellow decoction of the berries assumes an orange yellow tint with alkalis, which is not changed on the addition of an acid. Lime-water gives it a greenish hue, persulphate of iron a greenish yellow. Chloride of tin gives a greenish yellow colouration, and a slight precipitate.

Sir Robert Kane succeeded, some years ago, by treating the berries with ether, in extracting a substance, crystallising in fine golden yellow crystals, to which he gave the name *Chrysorhamnine*, and assigned to it the formula $C_{23}H_{11}O_{11}$. He found that, when a solution of this compound was boiled in the air or in presence of an oxidising agent, it became converted into a substance which he named *xanthorhamnine*, to which he gave the formula $C_{23}H_{12}O_{14}$.

Since then, several eminent chemists have examined into the nature of these colouring matters, among whom may be mentioned Gellaty, Bolley, and especially Lefort and Schützenberger.

From their researches the following facts may be

gathered. Lefort, in 1866, succeeded in isolating two colouring matters from the berries, which he named *rhamnagine* and *rhamnine*. Rhamnagine is soluble in water, and may be obtained under the form of crystals, while rhamnine is an insoluble yellow amorphous powder. In researches published in 1869, he found that rhamnagine was identical in composition with rhamnine, and that only a molecular change took place in the transformation of rhamnagine into rhamnine, such as we are all aware starch undergoes on conversion into dextrine. He supported this view by analyses, showing that both these substances had the same formula, namely, $C_{24} H_{32} O_{14}$. The researches of Schützenberger further proved that, under the influence of weak sulphuric acid, rhamnagine is decomposed into a peculiar sugar, and a substance to which he gave the name *rhamnatine*, thus showing that rhamnagine is a glucoside. The following formulæ show the decomposition which takes place:—

$$\underset{\text{Rhamnagine.}}{C_{24} H_{32} O_{14}} + \underset{\text{Water.}}{3 H_2 O} = \underset{\text{Rhamnatine.}}{C_{12} H_{10} O_6} + \underset{\text{Sugar.}}{2 (C_6 H_{14} O_6)}.$$

From these results it would appear that the real colour-giving principle is rhamnagine, and that rhamnine and rhamnatine, which are insoluble in water, are only products of decomposition.

Decoction of Persian berries is principally used in print works for producing bright yellows and greens, on prepared tin cloth, in steam styles. To obtain yellows, the extract is mixed either with a little red mordant (sulpho-acetate of alumina) or with a little muriate of tin. The mixture is thickened, printed on, and the fabric steamed. To produce greens, the decoction of berries is mixed with prussiate of tin, the mixture is thickened and printed on the fabric, which is then steamed, when the yellow of the berries and the Prussian blue which is formed unite to produce green on the fabric. The decoction of berries is very apt to enter into fermentative decomposition, and thereby become ropy; this may be prevented by the addition of a little carbolic acid.

A very fine brilliant yellow lake is produced from a decoction of Persian berries, the manufacture of which was kept secret for a long period by the Dutch. It consists in adding pure carbonate of lime to the decoction, when the lime salt falls, carrying with it the colouring matter of the decoction. The yellow lake thus produced is moulded into small lumps, which are dried in the shade.

There is a variety of mignionette which used to be cultivated in England and France, called weld, its botanical name being *Reseda luteola*. This plant yields a most valuable yellow dye when fixed on wool by means of alum, not only because the colour is exceedingly brilliant, but because it is very solid, resisting light, heat, and acids. Alkalis only communicate to it a slight orange tint. Its colouring matter was extracted by M. Chevreul many years ago, and he gave it the name of *luteoline*. He obtained it in yellow transparent crystals. By the action of oxidising agents, such as bichromate of potash, it assumes a magnificent yellow tint, identical to that produced with it in cotton fabrics.

M. Moldenhauer has since studied luteoline, to which he assigned the formula $C_{20} H_{14} O_8$. It is slightly soluble in water, but very soluble in alcohol. It dissolves without decomposition in strong sulphuric acid, and yields, even when greatly diluted with water, a fine green colour with perchloride of iron. Schützenberger, who has lately studied this body, states that when mixed with water and heated to a temperature of 480° Fahr. in sealed glass tubes, it decomposes into what he considers pure luteoline and resin. The luteoline is found in crystals adhering to the sides of the tube, while the resin collects at the bottom. He states also, that if a decoction of the berries is boiled with weak sulphuric acid, a new yellow colouring matter is produced, which possesses a high dyeing power as well as a pure yellow hue.

The introduction of quercitron and flavine is the principal reason why weld has nearly disappeared from the market.

Aloes is imported into Europe from Bombay, Barbadoes, Jamaica, and the Cape of Good Hope, in the form of resinous masses, varying considerably in size. It is the dried sap or juice of several varieties of aloes, of the family of *Asphodels*.

Dr. Stenhouse, who has examined this substance, has succeeded in isolating two compounds; one, which crystalises in yellow prismatic needles, is soluble in cold water and alkalis, the solution having an orange tint. It has an intensly bitter taste. He has given it the name *aloïne* and assigns to it the formula $C_{17} H_{18} O_7$.

The second compound, which may be considered as the resin of aloes, has received the name of aloëtine. Dr. Schunck has produced from aloes a yellow dye, called *chrysammic acid*, which will probably be yet extensively used. It is prepared by heating in a water bath eight parts of nitric acid with one of aloes, when the violence of the action has ceased, a second part of aloes is added. The application of heat is continued, until hyponitric fumes cease to be given off. The mass is then poured slowly into a large bulk of water. The chrysammic acid falls in flakes to the bottom of the vessel. These are washed with water, until it assumes a fine purple colour. The formula of this acid is $C_7 H_2 2 (N O_2) O_2$. It forms small golden-yellow scales, soluble in alcohol and ether. Although but sparingly soluble in water, it communicates to it a magnificent purple tint, and its dyeing power is considerable. Mr. Saac has made a great number of dyeing experiments with chrysammic acid, and has produced with it a variety of shades. He believes that one day they will become commercial.

Turmeric is the root or underground stem of the *Curcuma tinctoria*, a plant which grows abundantly in the East Indies. It is imported principally from Bombay, Java, Batavia, and Barbadoes. That from Bombay is the most valuable. It is ground and sold to the dyers in the state of a fine powder of a remarkably brilliant orange hue, and of a strong odour. Vogel and Pelletier succeeded in extracting from it a colouring matter, to which they gave the name of *curcumine*. M. Lepage has, however, given the best process for its extraction. The ground roots are treated with bisulphuret of carbon, which dissolves a volatile oil and resinous matters. The root is then dried and acted on by a weak alkaline solution, which dissolves the curcumine. To liberate it, the alkaline solution is neutralised with an acid, when the curcumine falls as a precipitate. This is collected, dried, and dissolved in ether, from which it separates under the form of small, brown scales, which yield on trituration a brillant, yellow powder.

Turmeric is seldom used as a dye, owing to its colour being so easily affected by alkalis, a fact well-known to chemists, as they often employ it to ascertain the presence of a trace of free alkali or boracic acid in solutions. It is used in India to flavour rice, and by the natives to colour their skin.

Annatto is the pulpy part of the seeds of the *Bixia orellana*, which grows in South America. It is imported into this country from Mexico, Brazil, the Antilles, and especially from Cayenne, in masses covered with leaves, and varying in weight from 5 to 20 pounds. It is also imported in casks, weighing 4 or 5 cwt., as a homogeneous paste of the consistency of butter, and often having a repulsive odour of urine, which, it is stated, is added by those who store it, to keep it moist and to impart to it a richer hue.

At Cayenne, when the fruit of the bixia is ripe, it is gathered, coarsely crushed, and thrown into water, where it remains for several weeks. By this means the pulpy matter is separated from the kernel. It is next strained through a coarse cloth, and the colouring-matter gradually subsides. It is then collected and the excess of water evaporated, until it assumes a pasty state, when it is

exposed to the atmosphere in the shade until sufficiently dry to be shipped. The powder so prepared, and especially at Cayenne, is comparatively inferior, owing to the mass fermenting and producing matters which prove injurious in the drying process. The following analysis may be taken as the average composition of such qualities of annatto :—

Water	72.25
Leaves...........................	3·85
Starch, mucilage, woody fibre......	18·30
Colouring-matter	5·60

$$\overline{100·00}$$

Some thirty years ago, a M. du Montel introduced at Cayenne some marked improvements in the manufacture of annatto. He suppressed the crushing of the seeds, separated the colouring-matter by water, and prevented the fermentation by the addition of some chemical fluid. By this means he obtained annatto in a minute state of division, and having a very beautiful red colour, which is imported into this country in the form of small tablets, which are much used for colouring cheese.

An alkaline solution of annatto gives an orange precipitate with acids, alum, or sulphate of protoxide of iron, a yellowish brown precipitate with salts of copper, and a lemon-coloured precipitate with chloride of tin.

The colouring-matters of annatto have been studied by MM. Chevreul, Kerndt, and Bolley. It contains two colouring-matters, one a yellow, which is soluble in water and alcohol but insoluble in ether, and which gives a yellow colour to cloth mordanted with alum. It has received the name *orelline*, and its formula is $C_{12} H_{22} O$. According to Kerndt's statement, however, it is only a product of the decomposition of the second colouring-matter, the real colour-giving principle of annatto being *bixine*, $C_5 H_6 O_2$. Bolley proposes the following method to obtain bixine :—The best quality of annatto from Cayenne, after having been washed and dried, is boiled with concentrated alcohol; the alcoholic solution is evaporated to dryness, and placed to digest with ether, which dissolves a part of the residue, leaving a bright red powder, insoluble in water, but soluble in soap and alkalis, to which it imparts an orange tint, and yields a dark blue colour with sulphuric acid.

The use of annatto in print and dye-works is rather limited, its chief employment being to modify the shades of other dyes, such as certain tints of yellow produced by fustic or quercitron. It is also used to give a bottom to cotton before it is dyed with safflower or cochineal. In the production of oranges in steam styles, annatto is now entirely superseded by *aurine*, a colour derived from carbolic acid. It is still often used in dyeing a low class of cotton yarns. The yarn is dipped in an alkaline solution of annatto, and then passed through a weak solution of oil of vitriol, which precipitates the bixine in the fibre. It is then only necessary to wash the cotton to complete the operation. If an orange-yellow tint is required, the cotton is previously mordanted with tin.

Ilixanthine is the name given to the pale primrose yellow crystals obtained by Dr. Schunck from the leaves of the *Polygonium fagopyrum*, or common buckwheat. This body, to which he gives the formulæ $C_{30} H_{20} O_{20}$, is only sparingly soluble in hot and cold water, but more soluble in alcohol. Strong sulphuric acid changes its colour to a deep yellow without decomposition. It yields on a piece of calico mordanted with alumina a dark yellow colour, with tin a light yellow, and with oxide of iron various shades of yellowish brown, according to the strength of the mordant employed.

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

especially admired from their remaining green in artificial light. They are not, however, now produced, as the colours were unstable, and Messrs. Guinon, Mamas, and Bonnet found that they could produce greens which maintain their colour in artificial light by first dyeing their silks in Prussian-blue, and then immersing them in an acidulated bath of picric acid. It is interesting to observe that, if indigo be substituted for Prussian-blue, the colour appears blue by artificial light.

Lo-kao is the only substance with which I am acquainted, capable, with proper re-agents, of producing the seven colours of the spectrum.
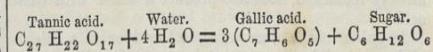
M. Charvin, of Lyons, obtained lo-kao from a weed indigenous to Europe—the *Rhamnus catharticus,* and received for his discovery a gold medal, worth 6,000 francs, from the Chamber of Commerce of Lyons. All these vert-lumieres are, however, now replaced by the brilliant greens obtained from aniline.

Tannin matters can be divided into two classes, those which give a blue-black precipitate with persalts of iron, such as gall-nuts, sumach, divi-divi, myrobalans, and valonia, and those which give a green colouration with persalts of iron, such as catechu, gambier, gum kino, and elder, larch, and willow barks.
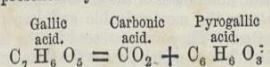
The first class are characterised by containing two acids, which have received the names of tannic and gallic acids.

Tannic acid, which is the all-important compound in this class of substances, was extracted some years ago by the following simple process, devised by M. Pelouze. It consists in treating in a displacement apparatus, coarsely ground gall-nuts with ether, which has been previously well shaken with water (during this process it has taken up one-tenth of its weight of the water). The ethereal solution, on being allowed to stand, separates into two layers, the upper one being nearly pure ether, and the lower one being an aqueous syrupy solution of tannin, which only requires to be evaporated in a water bath to obtain the tannic acid as a pale yellow spongy mass, inodorous, and having a most astringent taste. As is seen by the process of extraction, it is soluble in water, but insoluble in ether. It is soluble in alcohol. It is characterised by giving a blue-black precipitate with persalts of iron, but none with protosalts, and a white precipitate with tartar emetic or salts of lead. It gives a precipitate with gelatine and the vegetable alkaloids, and turns rapidly brown or black in presence of air and caustic alkali.
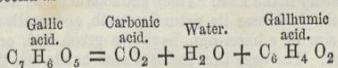
Tannic acid is a glucoside, decomposed by acids into a peculiar sugar and gallic acid, as seen by the following formulæ :—

$$\underset{\text{Tannic acid.}}{C_{27} H_{22} O_{17}} + \underset{\text{Water.}}{4 H_2 O} = \underset{\text{Gallic acid.}}{3 (C_7 H_6 O_5)} + \underset{\text{Sugar.}}{C_6 H_{12} O_6}$$

Gallic acid presents itself under the form of fine, white, silky needles, and is soluble in water, alcohol, and ether. Under the influence of a temperature of 410° F., it unfolds itself into carbonic acid and a beautiful white crystalline compound called pyrogallic acid, which has of late years been extensively employed in photography. If the temperature be raised to a higher point than the one above mentioned, gallic acid is decomposed into carbonic acid, water, and gallhumic acid. The first decomposition may be represented by the formulæ—

$$\underset{\substack{\text{Gallic} \\ \text{acid.}}}{C_7 H_6 O_5} = \underset{\substack{\text{Carbonic} \\ \text{acid.}}}{C O_2} + \underset{\substack{\text{Pyrogallic} \\ \text{acid.}}}{C_6 H_6 O_3}$$

the second as—

$$\underset{\substack{\text{Gallic} \\ \text{acid.}}}{C_7 H_6 O_5} = \underset{\substack{\text{Carbonic} \\ \text{acid.}}}{C O_2} + \underset{\text{Water.}}{H_2 O} + \underset{\substack{\text{Gallhumic} \\ \text{acid.}}}{C_6 H_4 O_2}$$

Gallic acid has been produced artificially by the action of potash on a di-iodosalycilic acid. When sulphuric acid is made to act on gallic acid, it transforms it into a red acid called rufigallic, which has the formula

$C_7 H_4 O_4$. When in the contact with alkalis, in presence of air, gallic acid, like pyrogallic and tannic acids, and various other organic substances, rapidly absorbs oxygen, as was shewn by M. Chevreul in 1820. On this fact, Liebig in 1838, founded an elegant method of determining the amount of oxygen in a mixture of gases. The process is however, only approximately correct, as I proved in 1863, that under these circumstances oxide of carbon was liberated.

Gallic acid gives a purple-black precipitate, with per-salts of iron, but none with the proto-salts. It gives no precipitate with gelatine, which is a most important fact, as I shall now proceed to show.

Tannin matters, such as oak-bark, are employed for tanning leather, and the conversion of a hide into leather depends on the gradual transformation of the animal matter which it contains into gelatine. This combines with the tannic acid, producing an insoluble compound which fills the pores of the animal tissue, and thus contributes, not only to prevent its putrefaction, but to render it impermeable to water. The value, therefore, of a tannin matter, depends on the amount of tannic acid it contains, the gallic acid taking no part in the tanning of the hide.

Tannin substances, such as gall-nuts, sumach, or bark, contain a ferment, which is susceptible of unfolding the glucoside tannic acid into sugar and gallic acid. It is necessary, therefore, that the tanner take great care in the management of the vats, to prevent any fermentation, especially the one called ropiness, for in such a case the vat would become useless. As it is a difficult matter often in summer to prevent this state of things, I may state that I have found that the addition of a few thousandths of carbolic acid is sufficient to prevent these chemical changes, without interfering with those which must take place in the hide.

Tannin matters, as you are aware, are much employed for producing blacks on fabrics, mordanted with per-oxide of iron. I asked myself some years since, whether it was the tannic or the gallic acid which produced the black, or if both participated in its production, and the results of my experiments clearly proved that tannic acid alone took part in its formation. This may be seen if two pieces of calico mordanted with iron, are dipped, the one in a solution of tannic acid, and the other in a solution of gallic acid. Both pieces at first become dyed, but after a few days, the one dipped in tannic remains black, while in the one dyed with gallic acid the colour has disappeared, the gallic acid having reduced the per-oxide of iron to the state of protoxide, which, as I have already remarked, does not produce a black with these acids.

As gallic acid is of no value to the dyer as a colour-giving principle, he must take care that his tannin matters, such as sumach, are carefully stored and kept dry, so as to avoid any gallic fermentation taking place, which would decrease the amount of tannin they contain. He should also avoid holding a large stock, as the fermentation above mentioned slowly proceeds in the tannin matters, as is proved by the fact of sumach, for example, decreasing considerably in value, after it has been some time prepared.

I shall now proceed to give you a brief outline of the characteristic differences of the several tannin matters.

Gall-nuts are the most valuable and important of all tannin matters. They are produced by the female of an insect called *Cynips*, which pierces the buds on the young branches of the *Quercus infectoria*, a tree growing especially in the East. There she soon deposits her eggs, and the bud loses its natural growth, and swells out to the size of a hazel-nut, having a green, red, or pink colour. The eggs thus inclosed soon hatch, and the insect undergoes all its metamorphoses until it attains the perfect state, when, if allowed (which is not to the interest of either the gatherer or consumer), it makes a hole and escapes. Good gall-nuts should not be so pierced, and they should be heavy, and of a fresh green colour. If the insect has escaped they are yellow, and are not nearly so good quality.

In the market, they generally bear the name of the port from which they were shipped. Thus, there are Aleppo gall-nuts, which are considered the best in the market, then the Morea, Smyrna, &c.

The following may be considered as the composition of an average sample of gall-nuts :—

Tannic acid	65·0
Gallic acid	2·0
Ellagic acid }	
Luteo-gallic acid }	2·0
Chlorophyl and volatile oil	·7
Brown extractive matter	2·5
Gum	2·5
Starch	2·0
Lignine	10·5
Sugar, albumen, &c., and ash	1·3
Water	11·5
	100·0

Gall-nuts are employed to produce blacks on silks, in the preparation for Turkey-red, to produce fast blacks in calico printing, and lastly, large quantities are used in the manufacture of pyrogallic acid, the consumption of which in the present large requirements of photography must be enormous. We shall see, as we proceed, that gall-nuts are the only available tannin matter for the production of this acid.

An inferior quality of gall-nut is also sold, which is found on the *Quercus rubur*, which grows in Hungary, Styria, Croatia, and Piedmont. It is used in those countries for tanning leather, and in some parts of Germany as a cheap substitute for the Eastern nuts.

Sumach is, as Dr. Stenhouse's researches show, the only substance in which the tannin principles are identical with those of gall-nuts, although in this tannin matter there is a comparatively large quantity of gallic acid. It also contains a soluble yellow principle.

Sumach is found in commerce as a coarse powder obtained by the trituration of the young branches and leaves of several varieties of the family *Terebanthaceæ*. The species most cultivated is the *Rhus coriaria*, which is a plant indigenous to Italy, Sicily, France, Spain, and Portugal. The shrub grows to a height of sixteen feet in the most arid soils, and is very extensively cultivated in some of those countries. The twigs and leaves are gathered once a-year.

Although sumach varies greatly in the amount of tannin it contains, there can be no doubt that from the *Rhus coriaria* is the best, whilst the most inferior comes from the south of France, and is the produce of the *Coriaria myrtifolia*.

In consequence of the powdered state in which sumach is sold, it not only varies greatly in quality, but is often deliberately adulterated with sand, or the leaves of other plants. It is easy to discover the sand, it being only necessary to put some of it in water, when the sand, from its greater specific gravity, readily falls to the bottom of the vessel. I will describe the method of determining the amount of tannic acid later on.

Extract of sumach is sometimes employed in print-works, to produce yellows with acetate of tin, blacks and greys with iron mordants, and dark yellow with sulphate of zinc. It is also used to produce blacks on woollen fabrics, although it does not give as good blacks as gall-nuts. Its principal use, however, is to mordant, either alone or in conjunction with salts of tin, the cotton warps of the mixed fabrics so extensively manufactured in Yorkshire, by which means the cotton takes the same colours as the woollen weft, both with vegetable dye-stuffs and those derived from coal-tar.

Sumach is too expensive a tannin matter to be used for the tanning of leather, but it is employed by the currier in the preparation of skins for dyeing with light shades.

Valonia is the acorn-cup of the *Quercus ægilops*, which grows in the isles of the Grecian Archipelago and on the coasts of Asia Minor. It is especially employed for tanning leather and adulterating garancine.

Divi-divi is the pod of the *Cæsalpina coriara*, and is chiefly imported from South America.

Myrobalans, which is largely used for tanning leather and producing blacks on wools, is the dried nut of the *Terminalia chebula*, and is imported chiefly from Calcutta.

Dr. Stenhouse has shown that the tannin matter of valonia, divi-divi, myrobalans, and oak bark are not identical with those of gall-nuts and sumach. They do not yield gallic acid when boiled with dilute sulphuric acid, but sugar and some other organic principle.

From the above facts, it must be obvious to all who use tannin matters, whether dyers or tanners, that these substances not only vary in value, according to the variety of plant from which they have been obtained and the country whence they are imported, but there are sources of deterioration which cannot be detected by the eye. Thus, for example, if a new sumach be mixed with a comparatively old one, it is impossible to detect the fraud. The only method, therefore, of ascertaining the value of a sample is to determine chemically the amount of tannic acid it contains. This may be done by the following process:—A weighed quantity (say 100 grains) of the substance to be tested is boiled with distilled water, and the decoction run off into a beaker, without filtering. This process is repeated four or five times. A test solution is prepared by dissolving one drachm of gelatine in four ounces of water, and adding 15 grains of powdered alum to the solution. 155 grains of this solution represent five grains of pure tannic acid. The test fluid is carefully dropped into the beaker until, on the falling of a drop upon the surface, the characteristic ring of tannate of gelatine is no longer produced. The quantity of test fluid used is then ascertained, and from this the amount of tannic acid is calculated.

Before passing from this class of tannin substances, there is one that I must mention, which has been used from the most ancient times, in Egypt, Arabia, and other Eastern countries, to dye wool, horse-hair, leather, &c. It is the leaves of the *Lawsonia inermis*, which appears to be the gopher wood of Scripture and the hennis of the Egyptians. The leaves are mixed with water, to form a paste of an orange-brown colour. This paste also is employed by the Asiatic ladies to dye the nails of their hands and feet, as well as their ears and hair.

Catechu, gambier, and *gumkino* are the most valuable of the tannin substances, which give a green colouration with persalts of iron. They are most extensively used to produce a great number of shades, varying from light drabs to dark brown, in cheap dyed cotton goods, such as fustians and corduroys. They are used in calico printing chiefly to produce browns, in silk dyeing to weight the silk, and in tanning to produce a low class of leather, easily distinguishable from that properly tanned with bark and other matters belonging to the first class, because when used for making shoes it communicates to the stockings a peculiar orange yellow hue.

For a long time there was much doubt as to the genus of plants from which catechu, gambier, and kino, which resemble each other very closely in their properties, were derived. M. Guibourt, a few years ago, solved the problem. He found that real *catechu*, *cutch*, or *Terra japonica* was the berry of the *Arica* palm. called *Areca catechu*, and the *Acacia catechu*, whilst gambier is extracted from the leaves of the *Uncaria gambir*, belonging to the family *Rubiaceæ*, and kino is obtained principally from the *Butea frondosa*, a leguminous plant.

Catechu is found in commerce principally in two states, the best in lumps varying in weight from 80 to 90 lbs., of a dull purple colour, and covered with leaves; the second, in masses, more or less covered with sand.

Gambier is imported into this country in the form of small cubes, having a yellowish brown colour.

Good catechu should not leave, on incineration, more than 4 or 5 per cent. of ash. Its aqueous solution should give, with alcohol or gelatine, an abundant white precipitate, with lime and baryta a brown precipitate, with salts of lead and tin a yellow precipitate varying in shade with the salts employed, and with bichromate of potash a brown precipitate. It should also take a decided brown hue with alkalis, and assume a greenish colour with salts of iron.

Catechu, besides naturally varying widely in quality, is freely adulterated with mineral substances, starch, tannin matters, and blood.

I have just stated the amount of ash a good catechu should yield. To ascertain the presence of starch, the sample should be first treated with alcohol, and the insoluble residue boiled with water, which will give a fine blue coloration on the addition of iodine if starch be present. The presence of any ordinary tannin matter in the catechu will modify the green coloration which the latter substance gives with the persalts of iron. Blood may be detected if present by treating the catechu with alcohol, and, after drying the insoluble residue, heating it in a tube, when ammoniacal vapours will be given off, as well as vapours of a most offensive odour.

Catechu is composed of three distinct substances, first, a tannin matter called *mimo-tannic acid;* second, *catechine*, or *catechinic acid;* and lastly, a brown colouring matter due to the oxidation of the catechine.

Mimo-tannic acid is prepared by treating pulverised catechu by ether in a displacement apparatus. The ethereal solution leaves on evaporation a yellow porous mass of this acid. Bombay catechu yields about 55·5 per cent. of mimo-tannic acid; that from Bengal, 48·2 per cent., while gambier yields from 36 to 40 per cent.

Catechine, or *catechinic acid*, is obtained by treating with boiling water the residue from catechu, which has yielded its mimotannic acid to ether. The water on cooling deposits a brown crystalline precipitate, which is re-dissolved in water and yields with sub-acetate of lead, and the precipitate washed. The lead compound is then suspended in water, and decomposed by sulphuretted hydrogen, when pure catechine remains in solution. Its formula is $C_{10} H_{10} O_4$. It rapidly becomes coloured brown in the presence of air, and an alkali, being, it is said, converted into *japonic acid*, whilst, with alkaline carbonates, it yields *rubinic acid*. It is also converted into japonic acid under the oxidising influence of salts of copper and of bichromate of potash.

If dyers, instead of employing catechu as imported, were to grind it, and wash with cold water, they would obtain an extract which would yield very pure shades of green drabs, while the insoluble residue of catechine would give a great variety of shades of brown. To increase the permanency of catechine colours, the goods dyed with them should be passed through a solution of bichromate of potash, as is usually done for catechu browns.

Dr. Stenhouse has shown that the tannin matters giving a green coloration with persalts of iron, such as catechu and elder and larch barks, do not contain a glucoside. The only exception he has found to this rule is willow bark.