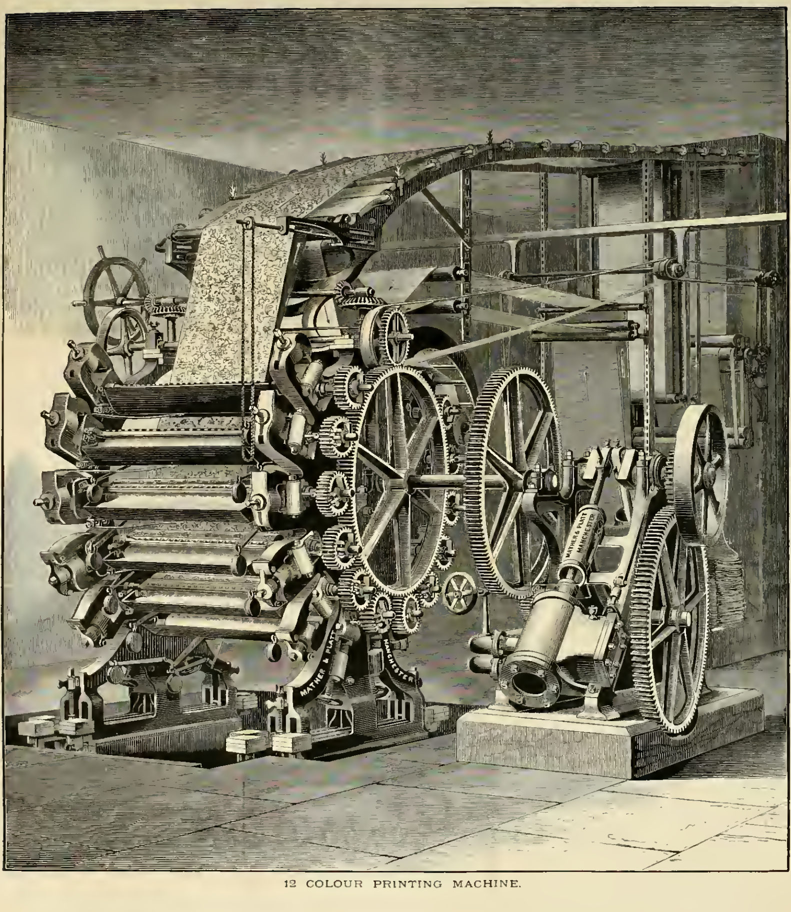
THE PRINTING
OF
COTTON FABRICS

ANTONIO SANSONE



12 COLOUR PRINTING MACHINE.

THE PRINTING OF COTTON FABRICS,

COMPRISING

CALICO BLEACHING, PRINTING,
AND DYEING,

BY

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PREFACE.

English technical literature is pretty rich in books relating to Calico Printing, but the standard works, such as the excellent handbooks by Crookes, O'Neill, and Calvert, are now somewhat out of date, the progress in this branch of industry having been very rapid during the last few years.

In compiling this work I have tried to bring all information up to the latest industrial methods and scientific discoveries, and have striven as much as possible to select only such matter as I thought to be of practical utility. At the same time it has been my aim to illustrate the principles of the different operations, and to give an outline of the theory of the fixation of the different colouring matters on the fibre, so as to embody both theory and practice.

The book contains also record of many of the lectures delivered by myself before the students of the School of Dyeing during my connection with the Manchester Technical School, and the majority of the processes have been tried on the printing machine and by my students in the laboratory. Some of the practical recipes have been published by myself in a series of articles which appeared in the *Textile Manufacturer*, on the testing of colouring matters in Printing, and I must tender my thanks to the proprietors of that Journal for allowing me to make use of them, and of other matters which I have previously published in their periodical, with the double object of exposing them to public criticism, and of having them to a certain extent checked by the experiments of my pupils. The recipes, however, must not be considered as fixed and unchangeable, but as guides or bases on which to work.

In the part relating to machinery I have tried to collect all the information concerning the apparatus now in use in the best works, and it is here, also, a pleasant duty to thank first of all the calico printing firms who have allowed me to visit their works on several occasions during the last two years; and, also, the machine makers for information kindly supplied to me, along with some of the diagrams and illustrations which appear in this work. I have tried, also, to illustrate the different styles and colours used in calico printing, and am enabled by the kindness and generosity of several eminent firms to furnish the book with the pattern sheets, which will be found at the end of this work. I have, also, to thank some of the firms already spoken of, and also many gentlemen who have been of much assistance to me in the preparation of this work, and I must not forget the manufacturers of dye stuffs, and their Manchester agents for valuable information and samples supplied to me by them on repeated occasions.

This book is only intended to illustrate the principles of bleaching and printing, with a short notice of the dyeing of cotton cloth, since the dyeing of fabrics generally has been so ably treated in Prof. Hummel's recent work on the dyeing of textile fabrics. Originally it was only intended to treat of the printing of cotton cloth, but a present of a set of printed patterns of woollen goods from a well-known continental chemist and calico printer, has brought about the insertion of a few of those patterns along with the other prints, and necessitated a short notice of the newest methods of printing woollen cloth.

In the theoretical part of the work the best methods of analysis or testing of the different raw materials have been indicated, and in treating of the different substances formulæ have been given of as simple character as possible.

Manchester, March, 1887.

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HISTORY OF CALICO PRINTING.

THE study of the tinctorial arts is not only of interest to the industrial world, but is also of historical interest, since in history we find that the highest political and commercial powers of nations, and consequently the highest degree of civilisation, have been connected with the greatest development in the production and colouring of the textile fabrics. This fact, if true for past periods of history, is especially striking in the middle ages, and certainly very striking at the present time, when we find that those countries which have made the greatest progress in tinctorial arts are also those which have attained the foremost rank in modern civilisation; and this gauge of the degree of civilisation, if correct for the arts of dyeing generally, applies in a special way to the industry of calico printing. And in fact there are few industries which require the same amount of skill and practical ability, combined with so much science and art, as this wonderful manufacture.

When we look at a print—especially a modern one—our attention may be directed to the beauty of the pattern, the brightness of the shades, or perhaps the happy combination of colours, but as a rule we are apt only to give a passing attention to it, so much have we been accustomed to see calico prints, and entertaining the idea that their production is one of the most natural things in the world; but only those who are acquainted with the subject can imagine the amount of labour, ability, and intelligence which has been bestowed upon them. Our modern prints represent the labour, experience, creative and inventive genius combined, of many centuries. By this I do not mean to say that the present generation has not had its share in the development and improvement of the industry; on the contrary, the most striking results have been achieved in modern times by bringing to bear upon it the brilliant discoveries and untiring labours of the scientific men of the present day. Further, a great impetus has been given to calico printing by the application of the wonderful mechanical inventions for which this century will ever be famous in the history of industry, and not least by the application of the principles of art to the designing of the patterns. The great merit of the modern industry of calico printing lies in the happy combination of science, art, and practical skill and experience.

The art of staining or producing designs on fabrics can be traced to very remote times, and it is by some authors asserted that it was practised 2,000 years before the Christian era. All writers on the subject are agreed in considering India as the birthplace of calico printing, but the earliest known historical record is from Pliny, from whose writings we gather that the Egyptians were very skilled in the production of patterns of different colours by applying or painting mordants on fabrics, and then dyeing by a colouring matter, which very likely may have been madder.

Indigo as a colouring matter has been known from the most ancient times, having very likely been one of the first which gave rise to the production of patterns, some of which even yet survive. One of the most primitive methods of producing patterns on fabrics is by binding some spots round with cord; when immersed in the dye bath the fabric is coloured all over except on the spots which have been tightly bound.

For some centuries the art progressed very slowly, as for a long time it was only possible to produce two or three colours on the same fabric at the same time, whilst the mechanical appliances have been correspondingly slowly improved until brought to their present state of comparative perfection.

Madder, although of not such remote employment as indigo, was also known in ancient times, and its introduction into European industry gave a great impetus to the development of the dyeing and printing trades.

As will be easily understood, the transformation which has gradually taken place in printing has been brought about either by the discovery or application of some new colouring matter, or by the improvement of mechanical means employed, or by the combination of the different colours on the same cloth, and in the production of varied coloured effects, which constitutes, in fact, the artistical part of calico printing. The mechanical means used in the production of patterns or designs were at first of a most primitive character. But the production of white spots or patterns on fabrics, which are afterwards dyed in the indigo vat by the resisting, or what we may call the reserving process, cannot be considered as a primitive process, since in this a much more advanced knowledge of the tinctorial arts was needed—in fact, it required the knowledge of the setting up and employment of the indigo vat, knowledge which could only be obtained by considerable progress in civilisation. White effects on indigo-dyed goods were produced principally by two simple methods which are yet employed by eastern nations, one of which consists in tieing up very tightly the spots which are to remain white, as referred to before. The other method relies on the employment of fused wax, which is put on the cloth in spots which are intended to remain white, and when the cloth is immersed in the indigo vat it is dyed all over except where the wax has been applied; the wax itself is removed afterwards by washing in a warm alkaline bath.

Employment of stencil plates to produce coloured patterns on white ground, the colour being applied by means of a brush, may be considered another stage of progress; but this method has never been extensively employed for calico. The introduction of the block in calico printing was a marked advance—in fact, it may be considered that since that time calico printing has really attained to the dignity of a great industry. By means of the block a large variety of patterns could be produced in different colours and design, and patterns could be properly and artistically executed. The perrotine, the forerunner of the roller printing machine, was an industrial adaption of the block printing, and the machine is even now employed in some works on the Continent. But the credit of the calico printing industry having attained such an important development is due to the roller printing machine first, and to the progress of chemical science afterwards.

The Indian printed, or rather painted, fabrics were known a long time in Europe before any attempt was made to imitate them. The exact date is not known when the art was introduced into Europe, but it is not unlikely that it was tried in several countries at the same time, judging by the records and the specimens in the different museums. At the beginning it was really painting rather than printing, and, in fact, in the French language the name of *L'Industrie des toiles peintes*, or *des Indiennes*, preceded that of *L'impréssion des Tissus*. It is stated that painted cloth was produced in London in 1410, but it is probable that it was linen cloth. The printing of linen and other fabrics, especially silk, was known in Europe previous to that epoch, as is proved by specimens of printed fabrics in the South Kensington Museum, among which is a specimen block produced in Sicily in the 13th century; but the production of printed cotton cloth was a later achievement. It is difficult, however, to be precise in the exact date or the country where it was first attempted. Judging by a Genoese square, a large printed pattern kindly lent to me some time ago by Sir Joseph Lee, of Manchester, the art of calico printing or painting was known in Italy in the 16th century, and probably even before this date. It is certain that printed calicoes were imported into England in 1627 by the East Indian Company, and that patents were granted in this country for the production of printed or stained fabrics in 1619, 1634, 1675, etc., mostly for linen, cotton cloth being mentioned, however, in the patent of 1634. In 1689 the manufacture of *Indiennes* was established in the neighbourhood of Neuchâtel, in Switzerland, and the old works are still existing, although the industry has left the place long ago. The Brothers Koechlin started cloth printing at Mulhouse in 1746, and in 1748 introduced block printing and the use of mordants. The first record we have of calico printing in Manchester is from 1763, while it was established in Scotland in 1738. Among the various difficulties and trials the industry had to submit to in its early days in this country was an excise tax of 3d. per square yard on all printed calicoes, which was imposed in 1702 and raised to 6d. in 1714; and curiously enough in 1720, a law was passed forbidding the wearing of printed calicoes, and cases are recorded of ladies being fined for the offence of wearing printed calico dresses. This law was partially repealed in 1736, when mixed goods were allowed, but still saddled with an excise duty of 6d. per yard. The prohibition was completely removed in 1774, but the duty was retained at 3d. per yard, to which ½d. was added in 1806; and it was not until 1831 that the tax was completely removed.

In 1830 the amount of printed calicoes produced in England was about 8½ millions of pieces, while in 1840 it rose to 16,000,000 pieces. The price of some prints in 1795 was as high as 2s. 6d. per yard.

The block, which in its most primitive form has been used from the remotest times among the Eastern nations, seems to have been employed in Europe for the printing of fabrics before it was used for book printing; but it is certain the introduction of the block in calico printing has asserted a very marked influence in its development. The block-printing machines, such as the Perrotine, etc., have no doubt also had a certain share in the progress of the industry, but it is due to the roller printing machines that it has attained the development which it now possesses.

The employment of engraved copper plates is a matter of great historical interest, for to this method was due the invention of the roller printing machine. The first attempt to print calico goods in England was made with the object of imitating the Indian fabrics, which were, early in the 17th century, largely imported into this country. First calico was imported from India and printed in this country; then yarns were imported, woven into cloth, and the cloth printed; and finally the cotton itself was imported, and the whole of both the manufacturing and printing processes gone through here, and therefore the history of the development of calico printing is doubly interesting, it having been the principal cause of the building up of the great cotton industry of Manchester and Lancashire generally.

The roller printing machine was introduced at the end of last century, the first patents taken in this country dating 1743 and 1772, being the first attempts in the application of the new principle of continuous printing. The invention is generally ascribed to Thomas Bell, who describes a six-colour machine in his patent dated 1783, when we find the "Doctor" mentioned for the first time; patents and improvements have followed each other during the course of this century, until the roller printing machines have been brought to the high state of perfection in which they now exist.

In France the roller machine was introduced in 1801, so that England has the priority in this important modern invention. The block in its improved form has been employed all along during the course of this century either alone or connected with the roller machine, and is even now employed in its most perfected form for the production of very fine and artistic prints in Alsace.

The Genoese square, alluded to before, is a large piece of print which was very probably used as a bed cover, or it might be as a kind of banner or piece of decoration, in the numerous religious feasts which were so much in vogue in Italy up to within a quarter of a century ago, and which still exist in some places. The design, which appears to have been produced both by hand, by the brush, and by the block, must have also been used in the repeating of the patterns; it is also probable that the stencil was employed at the same time. The design represents the trunk of a tree with branches, on which are arranged flowers, leaves, grapes, etc.; birds and butterflies being introduced on the tree and on the ground. The colours found on the pattern are principally red and pink for the roses and other red flowers, Indigo blue principally for the leaves and for blue flowers, then very dark purple or chocolate on the trunk, branches, etc.; then light purple and buff are also found, and a black, which, in reality, is a very dark purple, for the outlines of the different patterns.

The design contains a large border all round, consisting principally of flowers and leaves. The red and pink are undoubtedly madder red and pink on alumina mordants, while the black, chocolate, and purples have also been obtained on iron mordants alone or mixed with alumina. The blue is indigo; here it is of importance to note that while by some it is asserted that indigo was not known in Europe in the 16th century, this, however, is not the case, as indigo was in use in Italy already before that epoch, and, in my opinion, the Genoese pattern has been produced by direct application of reduced indigo, and not by woad, the dyestuff used in Europe before indigo was introduced.

If some enthusiasts are to be believed, roller printing will have at some future time to make room for the electrical processes both for producing patterns and colouring matters on the cloth. Still, as these are yet either only in the imagination, or in a very crude, experimental state, we must patiently await the revelations the future may have in store before accepting their views, though there is not much doubt that electricity will in future play an important part in the tinctorial industries.

Photography has also been repeatedly tried for producing patterns on fabrics, but the processes have never been found capable of being used on a large scale in an economical way.

Other methods of printing have been repeatedly tried and recommended, but only one or two have been found capable of utilisation, and even then in a limited scale, so that the roller printing machine is the one now mostly used in the production of prints. If we consider some of the most recent events in calico printing we will be struck at the thought of the complete disappearance of madder; this dyestuff, which only a few years ago formed such an important factor in the production of prints, has been completely driven out of the printworks, and replaced by artificial alizarin, and the madder cultivation which in France only amounted to about four millions of pounds sterling annually, is now almost a thing of the past. A certain amount of madder is still used in wool dyeing.

In reference to the production of turkey-reds, the principal improvements that have taken place are the employment of alizarin, and the introduction of the shorter process; the long process is, however, still employed, and the prints are still produced by the discharging method, although it has been repeatedly tried to produce them in a more direct way. The tendency of the industry is to produce the colours on the cloth by the direct printing process, and the steam colours have attained a great importance and a high degree of development, and it seems likely that in the future the steam colours will be more and more employed, and in preference to the dyed colours.

The introduction of coal-tar colours has effected great changes in the practice of calico printing, and rendered possible the production of more complicated patterns, and much brighter and greater variety of shades than could be done before.

Indigo, although seriously threatened by Bäyer's discovery of the synthetic production of indigotin, is as firmly established as ever, as the artificial product cannot be as cheaply produced as the natural dyestuff.

By looking at the patterns in vogue in the last few months it will have been observed that indigo blue and red have been very prominent, in other words, it is interesting to observe that after all we have gone back in these styles to the effects produced 2000 years ago by the Hindoos. We can produce brighter reds, and execute finer patterns, but the colours are just the same, although fixed differently.

The indigo blue, being fixed by the direct process, with a short steaming by the Glucose method, which, although patented in England in 1857, and in actual work in this country in the last few years, has been brought to great perfection of late in Germany.

One of the most important matters connected with calico printing is the improvement which have of recent years taken place in the machinery and plant used, and in this respect Manchester occupies the front rank, while the machinery produced here is largely used in the best works abroad.

Only a few countries have engaged in the calico printing industry. Of these England takes the leading part, as far as the amount of production is concerned; next the United States of America, the production of which is also very important, although mostly confined to common goods; then France, Germany, Switzerland, Austria, and Russia have each a considerable production of printed goods. Spain is also very well represented, whilst Italy, Portugal, and Belgium have not as yet taken up a very important position in calico printing.

The English industry is principally confined to the neighbourhood of Manchester and Glasgow. Manchester is the largest centre for the production of cotton prints, and, as said before, England is the largest producer in the world. It is probable that there are in and around Manchester at least 50 to 60 very considerable calico printing works, and the number of printing machines probably exceeds 500.

Mulhouse is still the leading centre for high-class printing, and the printing machines of Alsace were about 100 a few years ago.

A curious point connected with calico printing is that Paris still holds the monopoly for the production of designs, especially of those of the better class and of high artistic value.

BLEACHING.

Cotton in its natural state is principally composed of cellulose, and is accompanied by a small amount of natural impurities, which average about four or five per cent. Before any colouring matter can be successfully applied and fixed on the fibre, a preliminary cleansing and purification is necessary, and according to the process to which it has afterwards to be exposed the material must be subjected to a more or less thorough treatment; for instance, for the dyeing of plain dark colours, a simple boiling in water for the purpose of wetting is found sufficient, while for some other shades the material is scoured with alkaline solution, and for the production of light or bright hues a thorough bleaching is requisite. Cotton is very seldom bleached in the unspun state, although a previous bleaching before spinning might be found very beneficial for some special purposes, since loose cotton can be very readily bleached. Cotton yarn does not offer great difficulties in the process of bleaching, since it contains, in addition to natural impurities, very little of other impurities which might have been added during the spinning process, such as for instance a little grease and a small amount of dust taken up during the different manipulations.

Cotton cloth, on the contrary, contains a much larger amount of artificial impurities, added in the sizing of the yarn before weaving, and it offers, consequently, greater difficulties in the bleaching process.

As a general rule, in applying colours on cloth by printing, it is necessary to have the material as pure as possible in order to obtain bright colours, and hence the great importance of the bleaching process before printing.

Bleaching is nothing else but a process of purification;

it aims, in fact, at the production of a pure cellulose by eliminating the natural impurities, and in the case of cloth, also of the artificial impurities added in the sizing and weaving processes.

The theory of the bleaching operations will be understood when taking into account first of all the characteristics of cellulose itself, and then in considering the impurities accompanying the same.

CELLULOSE has attracted, of late, a great deal of attention at the hands of chemists, although the question is far from having been as thoroughly studied as it deserves to be ; and this more especially in regard to the natural impurities of the cotton fibre. In fact, since Dr. Schunck's investigations, nothing, or at all events very little, has been done in the subject, in all cases, very little additional light has been thrown on the matter.

Dr. Schunck estimated the substances which can be extracted from alkalies to be on an average from 3 to 5 per cent., of which 2 to 7 per cent. was obtained in the form of ash, containing iron, alumina, silicate of alumina, sulphate of lime, and sulphate of soda ; he obtained besides a waxy substance which he called cotton wax.

Cotton contains also fatty substances—margaric acid, &c., beside albuminoids, pectic and parapectic acid, and a mixture of both.

It contains, besides, a small amount of colouring matters which are the cause of the greyish yellow colouration of unbleached cotton. Consequently the bleaching operations consist of two distinct processes, the SCOURING or BOILING for the removal of impurities capable of elimination by means of alkalies, and then the BLEACHING for the destruction of the colouring matters.

We will, later on, come again on the explanation of the theory of the different operations ; for the present it will be necessary to note a few points of importance connected with the way the cellulose behaves when treated with different reagents, in order to be able to understand why those chemicals, now used in bleaching, and no others are employed, and also why they should be employed under certain conditions of temperature or strength.

CHARACTERISTICS OF CELLULOSE.

The cellulose of cotton is a white substance belonging to the class of carbohydrates, and possesses the empirical formula $C_6 H_{10} O_5$. It is insoluble in water, and in the majority of ordinary solvents; but it dissolves in strong sulphuric acid, both in the cold, and more especially by heating. Weak mineral acids have no effect on cellulose when employed in the cold, but they act injuriously when heating, or when employed too concentrated even in the cold, as for instance sulphuric acid, which would convert it into a kind of vegetable parchment. But weak solutions of hydrochloric or sulphuric acids of the strength employed in bleaching can be very safely used. Weak alkalies do not assert any injurious effect on cellulose, and can be employed even at the boil, and under pressure.

But concentrated solutions of caustic soda react on cellulose by mercerising the same. Milk of lime does not act injuriously, even at the boiling, and under great pressure, but it would assert a destructive action if, while boiling the material, it is exposed to air by coming out of the liquor in the boiling vessel.

A very interesting fact connected with the employment of weak acids is that cellulose has the property, when immersed in these solutions, to condense the acid within itself at the expense of the surrounding liquor, which is made weaker in consequence. This fact is of great importance in bleaching, because it shows the necessity of not using too strong acid solutions, and at the same time the advisability of not leaving the material too long in acid baths, which, although weak, will react in the long run.

Mineral acids assert also a very destructive action on cellulose when exposed to dry heat, even if in small quantity, for instance, cotton, impregnated with weak sulphuric acid, and dried either in a hot stove or cylinder, will be completely rotted.

Of the organic acids, acetic and tartaric acid do not react on cellulose, even if the material is exposed to steaming, while oxalic acid acts injuriously in the same way as mineral acids, and therefore must not be employed in the preparation of steam colours in printing.

Chlorine, in the form of a diluted dry gas, does not react on cellulose, but reacts in the presence of water by indirect oxydation, and no direct combination of chlorine with cellulose takes place. Hypochlorous acid and the hypochlorites in solution do not assert any injurious action when cold, but they act very strongly if employed in strong solutions.

A point of great importance is the conversion of cellulose into the oxydized product, oxycellulose, for instance when cotton is exposed to the action of bleaching liquor for some time, and in presence of air, as when immersed partially in a solution of bleaching powder, or, when immersed in the solution, taken out and exposed to the action of the atmosphere, it will be found that it has become to a certain extent rotted or disintegrated, when a change in composition has taken place, showing less carbon and more oxygen when subjected to a combustion analysis. These products of oxydation, which can be obtained also by other oxydizing agents, have been called oxycelluloses, and have been studied by Witz in Rouen, and Messrs. Cross and Bevan in this country, and some light has been thrown on the subject by the investigations of these chemists.

Among the most important properties of oxycellulose is the power of attracting basic colouring matters and other products from their solutions. The oxycellulose, in fact, reacts as a mordant for the basic aniline colours, and may attract vanadium from its solution.

The fact of oxycellulose attracting colouring matters, and therefore acting as a kind of mordant, is of great importance in calico printing, as it not only affects the shades produced, but it has also considerable influence in the production of good whites.

Although cotton yarn only loses about 5 per cent. in the process of bleaching, cloth is found sometimes which loses as much as 20 or 30 per cent., and even more; this of course is due to the weighting materials which are employed in the sizing process.

Although the bleaching process for cloth is, chemically speaking, the same, it varies in practice pretty considerably, in accordance with the cloth being intended to remain white and be sold as such, or being printed. For market bleach the white must be as perfect as possible, while for printing bleach it is necessary to have as pure cellulose as possible, and free from impurities, in order that no difficulty should be there in the clearing of the whites after printing.

In the bleaching process the natural impurities of the cotton fibre play a much more important part than is generally believed, and this influence is even more felt in the following dyeing or printing operations. For instance, a cloth may be thoroughly white, and yet not act sufficiently well in the madder or rather alizarin dyed styles, for which a special bleach is required—the so-called *madder bleach.* This point is of great importance in practice, since it affects very often the shades of red which are produced.

The following will give an outline of the bleaching process generally followed for printing cloth:—

BLEACHING PRINTING CLOTH.

The first operation the grey pieces have to undergo before they are bleached is the

STAMPING.—This is necessary in order that the goods can be recognised after they have been bleached. Then follows the STITCHING of the pieces to each other, end to end, in order to form a long ribbon, by means of which the cloth is treated in a continuous way.

As well known, cotton cloth contains on its surface a certain amount of light down, consisting of the ends of the cotton fibre, and this will have to be removed before the goods are bleached. The removal of this down is of special importance if the goods are afterwards intended to be printed, since these small filaments of cotton would interfere with the formation of clean prints.

This down is removed during the operation of

SINGEING.—This is performed on specially constructed machines, working on the principle of passing very rapidly the pieces over red-hot plates—revolving hot cylinders or gas-burners which only burn off the small outstanding filments without touching the cloth, if the operation is well conducted. The gas singeing machine is now mostly employed, but plate or cylinder singeing still does very good service, and among the newer methods recommended may be mentioned the singeing by electricity. In this case a platinum plate or wire is used, which is rendered red-hot by means of the electrical current, and the pieces pass rapidly over this, and thus become singed as by the ordinary methods.

In plate singeing the plate is made red-hot by means of free fire, while in the gas singeing machines a series of Bunsen burners are employed, forming a flame line over which the pieces are passed. As a rule the goods are singed twice on either side, and they are afterwards wetted in order to extinguish any burning filaments.

To give an idea of the speed the pieces are allowed to travel, it may be stated that as a rule 5,000 yards of cloth per hour are passed over the gas singeing machine.

The goods are next washed thoroughly on the washing machine, and then allowed to steep or lie in a heap all night; a kind of fermentation sets in, which allows the sizing materials to be removed, and if the pieces were heavily sized it is well to give a second washing before the

LIMING.—This operation consists in passing the pieces in a continuous way through milk of lime, the proportion of which has been so arranged that the cloth takes up about 5 per cent. of lime to the weight of cotton.

SCOURING OR BOILING.—The pieces are then brought into the kiers by means of machinery; in these they are so arranged that they fill up all the space of the kiers in a regular way, boys entering into the vessels and helping in the laying of the cloth in the apparatus by means of sticks.

As a rule all the operations of bleaching are performed on cloth folded up in the form of a rope, this being a very convenient form, especially for running the pieces from one apparatus or machine through the other, but in some cases the cloth is worked quite open, and spread out to its full width.

The KIERS are strong iron vessels worked by steam, in which the scouring operations are generally performed, they are, as a rule, constructed completely closed and made of strong material to stand a high pressure, but in some bleach-works no very great pressure is employed, and, in fact, low pressure kiers are used; in some cases no pressure is employed at all, and the kiers are altogether open.

In the closed kiers arrangements are generally devised for creating a circulation of the liquid through the mass of cloth. This is effected in several ways, either by means of injectors, or, as in the so-called Barlow kiers, by working with two apparatus alongside of each other, the liquor being forced by steam pressure from one into the other, made to react on the cloth, several hours, and very good results have been obtained by this system, which, although an old one, is still employed in many works.

Other arrangements have been also devised, such as creating the circulation by means of pumps or injectors, or by connecting a smaller closed vessel with one or two kiers; the liquor being allowed to go in, turn, and react on the cloth in the kiers, after having been drawn into the smaller vessel.

As can be readily seen the systems are various, but all aim at the same thing, viz.: to allow the lime liquor to come in contact with, and react on, all the cloth, and permeate it thoroughly.

Where no pressure kiers are employed very good results are also obtained by the employment of the open boilers for this scouring with lime; but one precaution must be taken in this case, that no cloth must be left out of the liquor

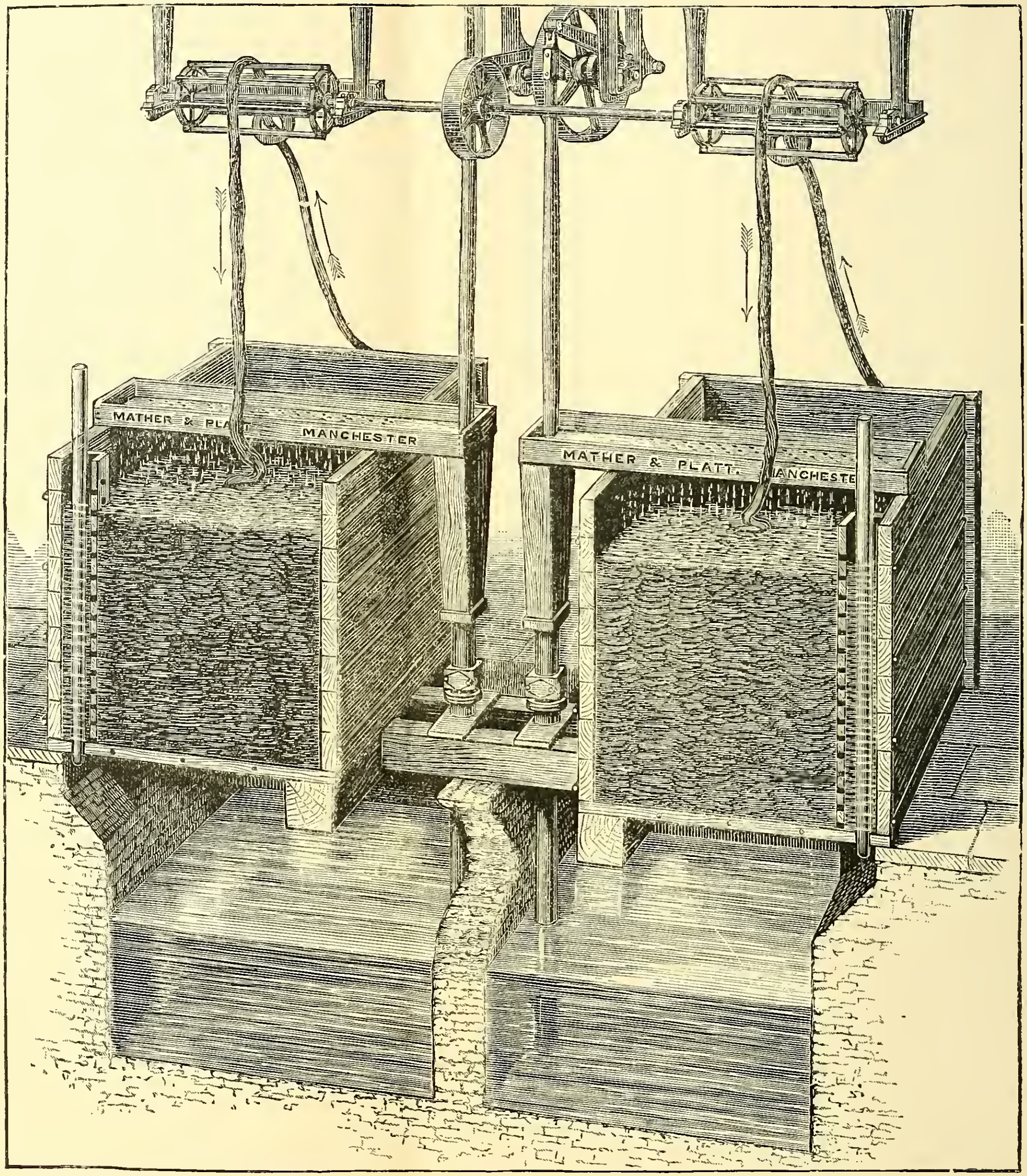


PLATE I.—BLEACHING AND SOURING CISTERNS.

exposed to air while boiling with lime, or it will become tender, and in some cases even completely rotten.

The pressure and the time required in this boiling of the cloth varies considerably in different works; some generally work 35lbs. pressure, some go even so high as 50lbs. to the square inch; while in the low pressure kiers 8 or 10lbs. is the rule.

The time employed also varies considerably; of course less time is required when working under high than under low pressure; in the former case some bleachers employ six hours, some more, some go up to the required pressure in the evening, stop the steam, and leave the pressure to go down of itself, taking out the goods next morning; while others boil their cloth for eight or ten hours at a moderate pressure, and then run off the liquor, adding cold water to the goods in the kiers before removing them. Whatever be the method used the pieces are generally subjected to a

WASHING, through an ordinary washing machine, in order to remove the lime and the impurities which may still be attached to the cloth. Then follows

THE SOURING, which is effected by means of muriatic acid of about 1 to 2° Tw.; the operation is performed now principally on mangles, or roller bleaching or washing machines, which are employed for the different operations of washing, souring, or even bleaching with chlorine liquor, &c.

This apparatus consists of a long cistern, made either of stone or wood, which is filled with the liquor; in this cistern is a wooden cylinder which revolves, and round it the cloth is wound in the form of a rope. Outside and above the cistern two wooden cylinders are arranged which act as squeezers, the top one pressing on the lower, and consequently on the pieces which in the form of rope pass several times between the cylinders; in going round the one in the cistern, the pieces are exposed to the action of the liquor, which is squeezed out of them, and falls back into the cistern. By the special arrangement of a plank with wooden pegs below the squeezers, the rope of pieces is directed in its course, so that it goes round in the form of a spiral, coming in on one side and going out again from the middle; in this way it does not get entangled. Two ropes are thus worked at the same time on the mangles, both entering on the sides, and passing out through the middle of the machine.

After the souring or passage through acids follows a thorough

WASHING.—This is performed twice, by passing the cloth in succession through two mangles or washing machines. The pieces are then brought again into the kiers to be exposed to another

BOILING, or scouring with soda ash and resin soap, for which about the following proportions are taken for every 100lbs. of cloth:—

5 to 6 lbs. soda ash.
$1\frac{1}{2}$ to 2 ,, resin (colophonium).

The soda ash and the colophonium are previously boiled for five or six hours with about

2 gallons (20lbs.) of water,

and when the solution is complete it is added to the kier, with the necessary amount of water, which is about one gallon of water for every 1lb. of cloth; in other words, the liquor in the kier is taken in the proportion of about 10 to 12, or even 15 parts of water to one of cotton.

This scouring is continued for five to six hours, at about 35 to 40lbs. pressure, and sometimes even more; but in the low pressure kiers, where the pressure is only allowed to go as high as 8lbs. to 10lbs., 10 to 12 hours are employed in the boiling; in the improved injector kiers three to four hours at 50lbs. pressure is stated to be sufficient. Here again the practice varies considerably in different works; in some cases no resin is employed at all, and caustic soda is used instead of the carbonate.

After this boiling the liquor is run off, and the goods are exposed to another

BOILING with about one per cent. soda ash to the weight of the cloth, for two or three hours.

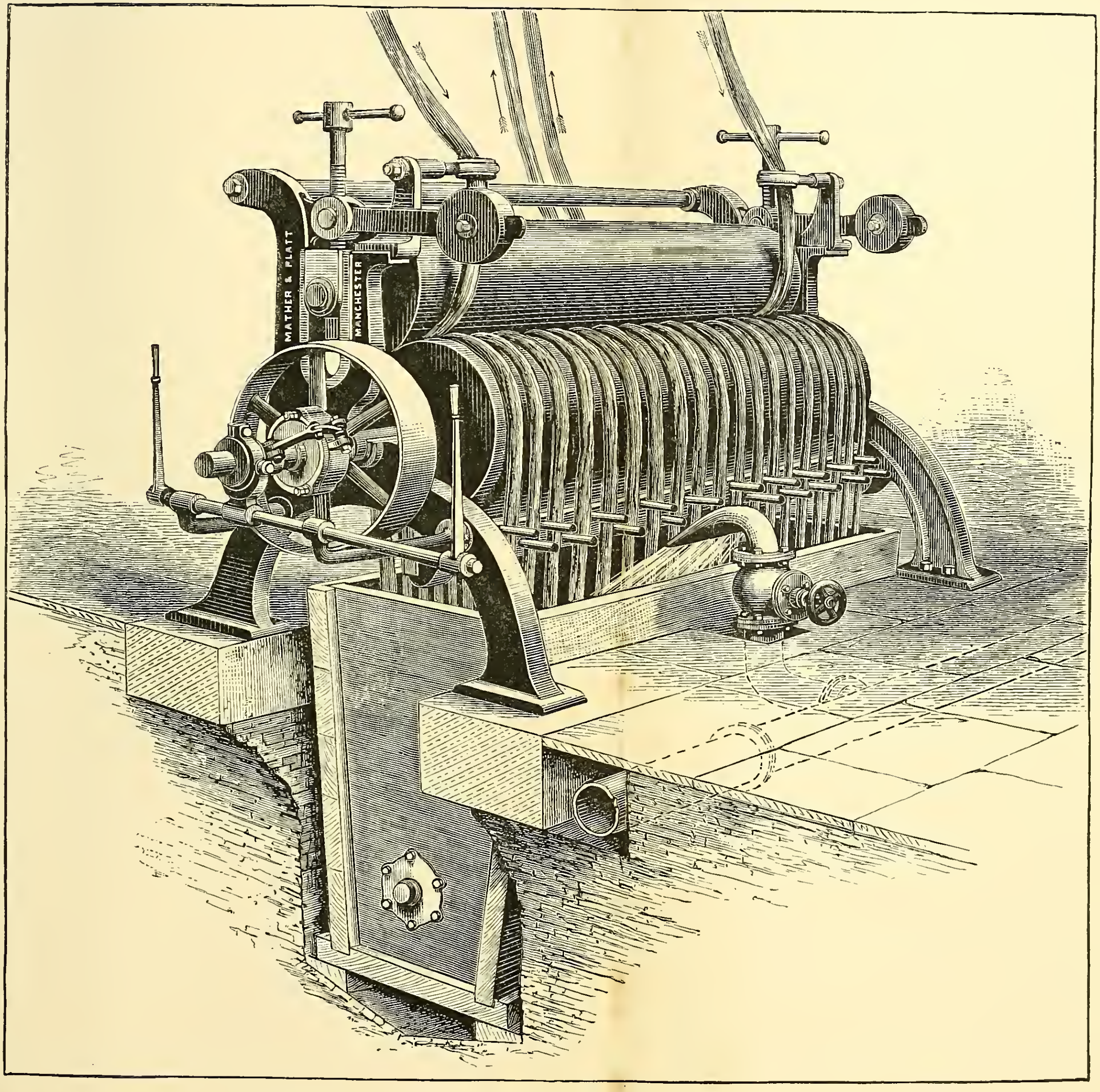


PLATE II.—ROLLER WASHING MACHINE.

A thorough Washing follows, and then the goods are ready for the real bleaching process, or what is generally called *chemicking*.

Bleaching is performed by means of chloride of lime solution; this is bought either ready made from the chemical manufacturers, or is made in the bleachworks by dissolving or treating the commercial bleaching powder with water.

The solution of the bleaching powder is generally performed in stone or iron vats or cisterns supplied with mechanical agitators, and in many cases also by resorting to a very simple contrivance in the shape of a revolving cask, perforated on its sides, and immersed partially in the water with which the cistern has been filled. The cask is filled with the bleaching powder and small stones, which, by the revolving of the cask, pulverize the powder, and cause it to be more easily dissolved.

Before use, the bleaching solution must be allowed to stand, or must be filtered, in order to make it perfectly clear, as there is danger of damaging the cloth by the particles which might otherwise be left in the liquor.

The strength of the bleaching liquor employed varies considerably in different works, and can be modified according to the length of time during which the goods are treated; as a rule it is advisable to use weak liquors and allow it to react longer, or rather to repeat the reaction, rather than to use strong bleaching liquors.

About 1° to 2° Tw. is a strength at which the goods can be safely exposed, but in many cases the liquor is only employed at $\frac{1}{4}$ to $\frac{1}{2}$° Tw. The liquor is applied cold, or may be slightly heated to about 20 to 25° C., when it penetrates the cotton better.

The method of application of the bleaching liquor also varies considerably; in some cases open cisterns are employed, in which the cloth is immersed and allowed to lie for several hours, while in other cases cisterns are used in which the circulation is effected by different mechanical arrangements, but as a rule mangles are largely employed now for the purpose. Close to these are placed the cisterns in which the pieces are laid after treating with bleaching liquor, and allowed to stand for two or three hours.

After the chemicking, generally follows a good

Washing, which is, however, omitted sometimes; then comes

The Souring (white sours), through sulphuric acid at 2° Tw.

Then comes a thorough washing, in which all traces of acid must be removed; and finally the

Opening up of the pieces and

Drying, principally on cylinders heated by steam.

If the goods are intended for printing they must be passed through the

Shearing Machine, in order to shear off any of the down or filaments brought out during the different operations, or not quite removed by the previous singeing process.

It must be observed that all large bleachworks have, along with the mangles or machines for doing the different operations of washing, souring, or chemicking, large stone cisterns, in which to keep the cloth, after coming out of one operation, and before being exposed to another.

Until now the strength of the bleaching liquors, or of the chemicking and souring solutions, have been indicated by means of the Twaddle, but this is not always a sure guide, and, therefore, more scientific methods of the estimation of the strength of the different chemicals must be employed.

SCOURING FOR TURKEY RED GOODS.

Goods which are to be dyed turkey reds or other plain shades are very seldom bleached, they are in fact only scoured or boiled by means of 3 to 5 per cent. of soda ash, or a corresponding amount of caustic soda, for three to four hours, once or twice; washed after each boiling and soured with sulphuric acid, at about 2° Tw., and finally thoroughly washed and dried, if they are not immediately dyed.

MARKET BLEACH.

The following course of operations has been successfully employed in Lancashire works for producing very good whites:

1 Lime boil or stew.
2 Wash.
3 Sour.
4 Wash.
5 Soda ash boil.
6 Wash.
7 Chemic.
8 Wash.
9 Sour.
10 Wash.
11 Soda ash boil.
12 Wash.
13 Chemic.
14 Wash.
15 Sour.
16 Wash and dry.

In market-bleaching the goods are afterwards finished, and in this case the blueing or tinting forms a very important part.

CONSIDERATIONS ON THE BLEACHING PROCESS.

In order to secure success in the manipulations of bleaching cotton cloth, it is necessary to pay attention to some points of great importance, which may otherwise be the cause of trouble and pecuniary loss.

The singeing operations do not offer any special difficulty if the proper machines are employed, and if well attended by practical workmen; in fact all the operations require skilled practical men.

The precautions in the boiling process with lime have already been mentioned, and the scouring operations generally do not offer any great difficulties. In the employment of acid and bleach liquors it is necessary that one or two facts should we well considered.

For instance it is absolutely necessary that every trace of acid should be removed by washing before the cloth is dried on the cylinders, or tins heated by steam, which are generally used for the purpose, or the acid will react on the fibre and decompose it. The cloth should also be as free as possible from chlorine, or rather hypochlorous acids, as the presence of hypochlorites will act injuriously, not only in the drying, but also when the bleached material is kept in stock for any length of time. In bleachworks where water is not very abundant, a less thorough washing at the end of the process can be used by employing a weak bath of bisulphite of soda, which will act as an antichlor, that is, it will completely neutralize the effect of chlorine, and at the same time remove any trace of hydrochloric or sulphuric acid, which latter, by reacting on the bisulphite, will drive off the sulphurous acid, which is innocuous.

A question generally asked is—which is the best acid to be used, hydrochloric or sulphuric ? It is more a question of price ; where the hydrochloric is cheap, it can be preferably used, while vitriol can be employed in localities where there is no Leblanc soda industry, and therefore scarcity of cheap hydrochloric. The reason why this latter is preferable is that it forms a soluble combination with lime, and therefore removes the same from the fibre ; while sulphuric acid, as is well known, forms the insoluble or rather partially soluble sulphate of calcium, which in many cases may be the cause of the hardness found in some bleached goods. By using mixed solutions of weak sulphuric acid and bleaching liquor, of the same concentration as they are used in bleaching, no precipitate, or at all events not a large precipitate, is formed, and that not at once apparent ; this explains why, notwithstanding the large amount of lime and sulphuric acid employed in the bleaching of cloth, the amount of lime or sulphate of calcium found on cloth is so small. No doubt any calcium sulphate formed remains in solution in the weak acid, or is mechanically carried away. It has been mentioned before that if cotton is impregnated with bleaching liquor, and then exposed to air, it is converted into oxycellulose; this should be borne in mind during the bleaching operations.

The employment of resinous soaps in the bleaching processes is also a matter of importance. Experience has established, without doubt, that it is of advantage in the production of good whites, and for cleansing the fibre, but it has never been satisfactorily explained how it reacts. It is also known that ordinary soap will act in the same way, and if it is not used it is on account of price. Probably the advantage in the use of soaps in the bleaching process lies in the fact that some of the natural impurities become soluble in soap solutions.

NEW BLEACHING PROCESSES.

Many processes have been recommended in the last few years, and many patents have been taken out; but so far very few have been found of real utility. As a bleaching agent nothing, up to the present time, can displace bleaching powder or the hypochlorites generally. For special purposes it may be advisable to employ another hypochlorite, such as soda or magnesia, instead of the lime salt, but in those cases it is the hypochlorous acid which is being utilised, and therefore there is no novelty in the chemical reaction. In fact, some new products advertised with so much flourish as new bleaching agents, are simply one or other of the hypochlorites

In the chemical bleaching process, we may say there is really no novelty, the apparent novelties being simply modifications in the way of employment. But it is different with the mechanical arrangements, these have been, and are constantly being improved, and progress in bleaching must be looked for principally in the improvement of machinery. Among the most noteworthy novelties in bleaching processes for cotton, are the following :—

1.—*The caustic-soda steaming methods and carbonic acid process*, comprising the so-called Mather-Thompson process.

2.—Lunge's patent method.
3.—Electrical processes, principal among which the Hermite method.
4.—Other processes of different origin, principally for the scouring of cotton before bleaching, in which petroleum or turpentine, &c., are employed, along with soap or alkalis.

THE CAUSTIC SODA STEAMING PROCESS.—The employment of caustic soda in the scouring of cotton is no novelty in itself, since caustic soda has been used in the scouring of yarns very successfully and regularly for many years, and if it is not employed for cloth by the ordinary scouring method in closed kiers, it is because it offers no advantage over the much cheaper lime, and is not so effective in cleansing the cloth, especially that intended for madder styles. It has been found, further, that it often causes spots in the cloth. But the exposing of cloth, impregnated with caustic soda, to the steaming, is a new departure in the employment of alkalis; it was originally brought forward and studied by Mr. Horace Koechlin, and then tried successfully in England, and this treatment forms the first stage of the Mather-Thompson process. The difficulties which have had to be overcome have been various, and one especially, a very important one, threatened for a time to put a stop to the employment of caustic soda and steaming combined; it was found that during steaming, if the cloth was exposed to air, a decomposing or weakening of cloth took place by oxidation; this drawback has been removed by the employment of some reducing agents along with the caustic soda, or by working in closed vessels at not too high a pressure, and keeping the cloth wet throughout.

MATHER-THOMPSON'S PROCESS.

This is divided into two distinct operations—the scouring or cleansing, and the bleaching proper.

SCOURING.—The pieces are stitched end to end in the ordinary way, so as to form a long rope, which can be

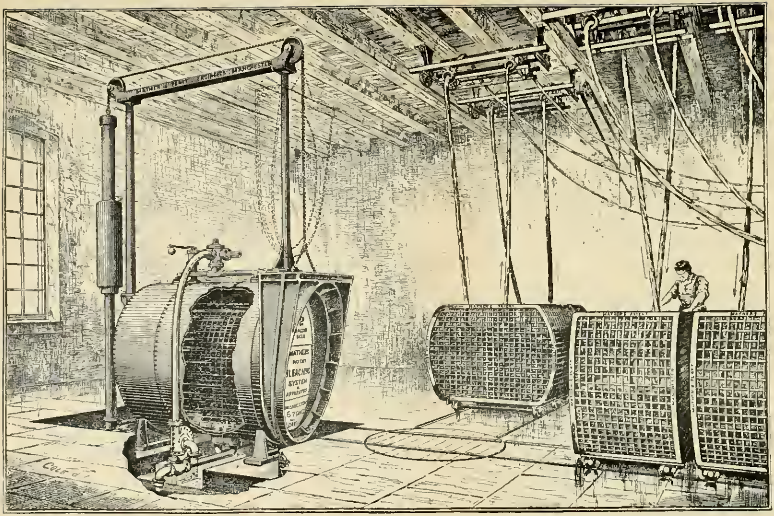


PLATE III.—STEAMER KIER, WITH CAGES.

worked in a continuous length, and then treated with the hot solution of caustic soda, which has been employed in the former operation of scouring in the steamer kier. It is then washed and brought into wagon cages, there folded by machinery, and the cages are pushed into the

STEAMER KIER. This consists of a horizontal boiler or cylinder, one end of which can be entirely closed by means of a stout wrought iron door, which can be lifted up and lowered by hydraulic arrangement. A centrifugal pump is connected with the top of the apparatus, which, by means of an inverted T pipe, fixed at the top of the steamer, and corresponding with the middle of each cage, allows a constant flow of the caustic lye on the cloth, through an arrangement of sprinklers, keeping the material constantly wet with the alkaline solution, and thus preventing decomposition. The caustic soda lye used in this operation is made up to 2° to 4° Tw., and will contain about ·5 to 1 per cent. NaOH; the pressure employed is 4lbs. to the square inch, and the duration five hours.

After steaming, the liquor is run off into a cistern below, and the kier is almost filled with hot water, which is kept in circulation by means of a pump, and thus washes the material. The water is then run off, the door opened, the cages removed, and the cloth rinsed with cold water, the scouring being complete.

The cages are constructed of galvanised iron lattice work, and are provided with a perforated column in the middle, by means of which the liquor can penetrate all through the cloth. Two cages will go into the steamer kier, and two tons of cloth can be treated at the same time. The cloth is worked either in the form of a rope or spread out in full width.

The steamer kier can be used in connection with the ordinary bleaching process; in fact, with a little modification, it can be employed as a boiling kier, the circulation being effected by means of a pump, and lime can be used for scouring in the ordinary way.

The Bleaching is effected in a series of troughs, as shown by the illustration, in about the following order:

Rinsing with hot water.
1st chemic bath.
Passage through carbonic acid chamber.
Washing.
Scalding with soda ash.
Washing.
2nd chemic.
Carbonic acid passage.
Wash.
Sour with hydrochloric acid.
Wash well and finish.

The cloth passes through the machine at the rate of 60 yards per minute. The novelty of this process is the employment of carbonic acid, which decomposes the lime hypochlorite, forming free hypochlorous acid, and effects the bleaching; but carbonate of lime is precipitated on the fibre, which must be afterwards removed by the bath of hydrochloric acid. A very quick bleach is effected by the process, as cloth only takes about 10 to 12 hours in all to go through the different operations, and a saving is effected in the amount of water used; a matter of grave consideration with bleachers who do not enjoy an unlimited supply of water.

The cloth is also not punished as much as in the old process, but it must be said that, although a good bleach for ordinary printing can be obtained by this process, the result is not quite so satisfactory for a madder bleach; this, however, might be overcome by modifying the process.

LUNGE'S PROCESS.

Prof. Lunge employs, for the purpose of increasing the action of the bleaching power, a reagent which, he asserts, has not been previously employed—viz., acetic acid, or any other similar weak organic acid, as, for instance, formic acid. The price of acetic acid is not a hindrance to its employment, because small quantities only are necessary, the acid

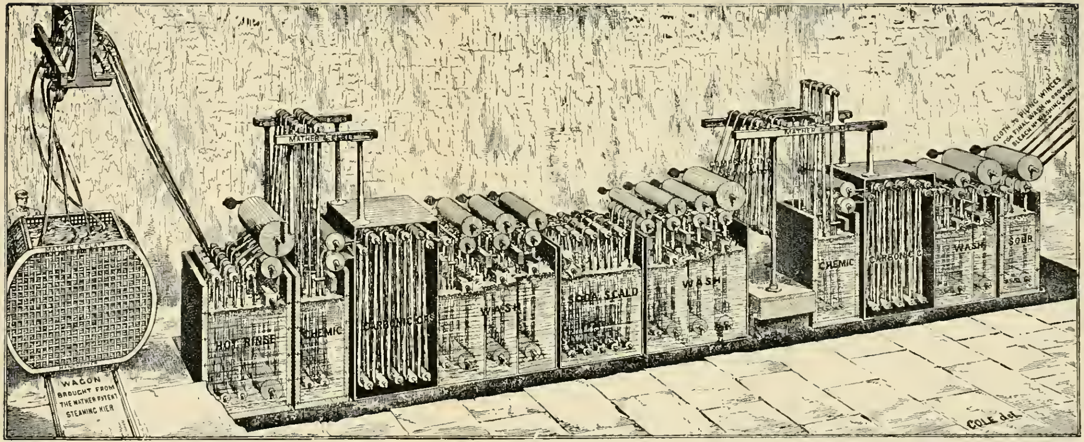


PLATE IV.—BLEACHING RANGE—MATHER-THOMPSON'S PROCESS.

being constantly regenerated. In the first case, chloride of lime and acetic acid give free hypochlorous acid and acetate of lime. During the bleaching process the latter, in giving up its oxygen, forms hydrochloric acid, which latter, by reaction on the acetate of lime, forms chloride of calcium and free acetic acid, which again reacts on the chloride of lime in the same way as before. Therefore a small quantity of acetic acid will be sufficient to effect the reaction. The hydrochloric acid which is formed during the bleaching process will never remain in a free state in the solution, because it reacts at once in the acetate of calcium to set free the acetic acid. This fact is of great importance, since muriatic acid reacts on the fibre if left in contact with it for any length of time, while, as is well known, acetic acid is completely harmless. As no insoluble lime salts are formed, the souring operations, which generally follow the bleaching, can be well dispensed with; in this case there will not only be a positive economy, but there is also no danger of any mineral acid being left on the fibre by imperfect washing, and therefore no fear of destruction of the materials, which sometimes occurs with very thick cotton goods. Acetic acid does not act injuriously even at high temperatures.

Acetic acid, or any other suitable organic acid, can be employed in different ways, viz:—by adding acetic acid to the bleaching liquor at first; by a passage through a very weak acetic solution, after the customary treatment in bleaching liquor; or by bringing the goods into water very slightly acidulated with acetic acid, and in which the bleaching liquor is gradually being introduced by causing the liquids to circulate on the bleaching material. It is stated that if the process be well conducted a saving in the amount of bleaching powder is effected, with the advantage that the water courses are not so much polluted. If the material to be bleached still contains alkali from the scouring process, or if the water is very hard, or the bleaching solution contains a certain amount of caustic lime, a larger amount of acetic acid will be required for the neutralisation of the bases, before the hypochlorous acid will be set free. In this case it is well to neutralise the free alkali or lime very carefully beforehand, by means of either sulphuric or muriatic acid, and then the necessary amount of acetic acid can be added to produce the reaction. The process is suitable for the bleaching of vegetable fibrous materials, either in the loose (raw) state, or as yarn or cloth, and also for the bleaching of some coloured goods, such as alizarin red and other coloured materials.

ELECTRICAL BLEACHING PROCESSES.

These have attracted in the last few years considerable attention, and several methods have been recommended, mostly relying on the decomposition of chlorides by the electric current, when a solution is obtained, probably of hypochlorous acid, which will then react in the ordinary way.

Among others the process of Hermite utilises the magnesuim chloride; others recommend calcium chloride, and others again common salt, while some would simply propose to decompose water by electricity, and utilize the oxygen as it is being formed. It is too early yet to say anything definite about any of these processes, which are still in the experimental stage; it is, however, likely that electricity will play a very important part in the bleaching processes of the future, although now the cost price is too high to allow it to compete successfully with bleaching powder produced by the ordinary chemical processes.

TESTING BLEACHED CLOTH.

A properly bleached cloth should not only show a good white, but must be free from spots or speckles, and it must also be suitable for the purpose for which it is intended. Of course, if it has been weakened during the process, it means that it is almost valueless. If any chlorine is left in the cloth, it will be at once perceived by the smell, while any free acid can be detected by soaking the cloth in water, and then testing the solution with an indicator; if the amount of acid should be in sufficient quantity to react on it, which is very seldom the case. It is advisable, in order to see if any oxycellulose has been formed, to dye a fent in a weak bath of methylene blue, which would be fixed on the fibre, as the oxycellulose reacts as a mordant.

A more important test is, however, to see if the cloth is suitable for madder styles or for alizarin dyed colours. Cloth, properly bleached, or a good madder bleach, will not only produce a good red, but will allow the whites to be cleared well, while sometimes a cloth may be very well bleached, and show very good whites after printing, and yet not produce good reds. This test cannot be properly made in a laboratory, but must be made in the works by comparison. A fent of the bleached cloth to be tested is stitched to another of well known bleach, the same red mordant is printed on both, and then it is aged, dunged and dyed in the ordinary way. It will be seen afterwards by comparison if the two fents behave in the same way.

In the laboratory, tests in the same manner can be made, but they do not as a rule turn out satisfactory; for instance, the same mordant can be printed on by a small printing machine, and then dyed, &c., or the two fents may simply be worked in a bath containing alizarin, or a bath prepared as for alizarin dyeing, then washed and soaped to see how the white comes out; but it is never so satisfactory as a practical test made in the printworks.

CHEMICALS EMPLOYED IN BLEACHING.

ALKALIES.

Hydrated, Slacked Lime, $Ca\ (OH)_2$.—Carbonate of lime, $CaCO_3$., in the form of limestone, is found very plentifully in nature, and it is utilised for the production of lime, or oxide of calcium, CaO. by burning, or rather subjecting the same to high temperature in properly constructed kilns, when carbonic acid is driven off and burnt lime or CaO is the result.

$$CaCO_3 = CO_2 + CaO.$$

This oxide of calcium attracts water very eagerly, and is converted into slacked or rather caustic lime, $Ca(OH)_2$., by the following reaction:—

$$CaO + H_2O = Ca(OH)_2$$

The burning and afterwards the slacking of lime are operations which are generally conducted on a very large scale, and by very simple means.

The slacking of the lime is generally performed either in pits or in wooden vats, by simply throwing the burnt lime into the water and agitating with poles or sticks; sometimes iron vessels are employed with mechanical agitators. But on a small scale it is advisable to put the lime to be slacked, in broken up pieces, into an iron, earthenware, or even wooden vessel, and then to pour water on in small quantities at a time. When the lime is freshly burnt a very quick reaction will take place, and the lime will be easily slacked. It can be made afterwards into so-called milk-of-lime by adding more water and agitating.

In the use of lime two precautions must be observed—firstly, the stone must have been freshly burnt, or else, by long exposure to air, especially to damp atmosphere, the oxide of calcium attracts carbonic acid, and is converted again into the carbonate, which is inert, and quite useless for the purpose of scouring. In the second case the slacked lime must be quite free from lumps or stones, and before use it is always well to have it sieved. Lime is scarcely ever tested before use, but it can be tested—1. By titration with normal hydrochloric acid. 2. For carbonic acid, qualitatively and quantitively by adding acid to drive off the carbonic acid, which can be estimated.

CARBONATE OF SODA (Na_2CO_3) is produced on a very large scale in the alkali works by two processes, viz., the old Leblanc and the newer ammonia or Solvay soda process.

By Leblanc's method common salt is converted into sulphate of soda by treatment with sulphuric acid, when hydrochloric acid gas is obtained as a bye-product, and is dissolved in water, and sold under the form of commercial hydrochloric or muriatic acid.

The reaction can be illustrated by the following equation:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

The sulphate of soda is then treated in suitable furnaces with limestone and coal, when, by a series of reactions, the carbonate of soda is produced; the sulphate is reduced to sulphide by carbon, thus :—

$$Na_2SO_4 + 2C = 2CO_2 + Na_2S.$$

The sulphide in contact with the carbonate of lime gives carbonate of soda, and sulphide of calcium,

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The excess of carbonate of lime by the action of carbon and heat is reduced to the oxide,

$$2CaCO_3 + 2C = 2CaO + 4CO,$$

and the end of the reactions are mainly Na_2CO_3 carbonate of soda, and $CaS + CaO$, with some other minor products. By extracting with water, the carbonate of soda is dissolved, while the oxysulphuret of calcium remains, and goes to form those enormous and ever increasing heaps of strong smelling residue which are to be met with in the neighbourhood of all alkali works where the Leblanc process is used. The Leblanc carbonate of soda comes into commerce in three forms :—

1.—As soda ash.

2.—As soda crystals,

$$Na_2CO_3 + 10H_2O.$$

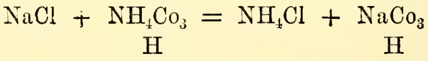
3.—As crystal carbonate, with less water of crystalisation.

Soda Ash is now generally sold at a given standard of strength, principally under the denominations of 48 or 58 per cent. The lower qualities are contaminated more or less with some of the products through which it has passed in the process of manufacture.

In some varieties a pretty large percentage of caustic soda is found; this for the scouring process is no detriment, but is in fact an advantage, while for special purposes the presence of caustic is objectionable, and therefore a purer product must be employed. Sometimes sodium chloride is added by the manufacturer to dilute the soda ash to the given strength, and sodium sulphate is also found in small quantity in the soda produced by the Leblanc process.

Among other impurities may be mentioned that of sulphides, and especially of iron. The latter is for many purposes very objectionable, and therefore products containing the same must be avoided, as the presence of iron in soda ash has been the cause of stains in the scouring processes. In testing soda ash the amount of pure alkali (Na_2O) must be estimated; this is done by the usual methods of quantitative chemical analysis well known to chemists, which need not be described here, sometimes, besides the total alkilinity, it is necessary to estimate the amount of free caustic soda—this also offers no difficulty in the practised hand of the analytical chemist.

Ammonia Soda comes generally in commerce in a pure state, free from caustic soda, and, of course, also from sulphates, as it is obtained by a direct process, viz—the action of carbonic acid and ammonia on a strong solution of common salt; when in the first instance, bicarbonate of ammonia is formed, which, in contact with the salt, forms bicarbonate of soda and chloride of ammonium.



$$NaCl + \underset{H}{NH_4Co_3} = NH_4Cl + \underset{H}{NaCo_3}$$

The bicarbonate of soda is precipitated and the chloride of ammonium remains in solution. After separation the bicarbonate of soda is dried, exposed to high temperature, and decomposed

$$2NaHCo_3 = Na_2Co_3 + H_2O + Co_2$$

neutral carbonate being formed, and the carbonic acid driven off, and utilized again in the following operation.

The chloride of ammonium, by treatment with lime, yields ammonia, which is utilized as follows:—

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

As will be readily understood, the carbonic acid and the ammonia are used over and over again, of course with a little loss, in the case of ammonia particularly.

In this process the only waste product is chloride of calcium, $Ca\,Cl_2$, which, so far, has remained unutilized, although great efforts are being made to obtain either hydrochloric acid, chlorine, or even bleaching liquor from it by commercial processes.

Soda Crystals.—Ordinary soda crystals

$$Na_2Co_3 + 10H_2O$$

form large transparent prisms of the monocline system, soluble in 1½ parts of water.

On account of the large amount of water of crystallisation it is a more expensive product than soda ash, or even ammonia soda, and consequently only used for purposes where a product of great purity and free from caustic soda is required, as for instance in the scouring of wool.

If intended for use in alizarin red or pink dyeing, it must be quite free from iron.

The commercial value of the soda crystals lies in the amount of carbonate of soda, Na_2CO, which they contain, and in their great purity, which causes them to be preferred for some purposes, even if they are more expensive, as for household washing, &c.

Crystal Carbonate of Soda has been introduced in the last few years, and is a product of great purity, containing less water of crystallisation than the ordinary soda crystals, and consequently the expenses in carriage are not so heavy as in the ordinary crystals.

This product, which has been introduced into commerce by Messrs. Gaskell, Deacon & Co., shows the following analysis:

Carbonate of soda	82·
Caustic soda	·—
Sulphate of soda	traces.
Sodium chloride	·25
Water	17·5
	99·75

so that it is a product of great purity, containing 82 per cent. Na_2CO_3.

Caustic Soda ($NaOH$), which is coming constantly more into use in the scouring and bleaching of cotton, especially yarns, is also largely used for linen bleaching. It is manufactured in very large quantities by the Leblanc soda process, and is brought into commerce either in liquid form in carboys, in solid form in iron drums, or in the form of a powder. Carbonate of soda, when treated with caustic lime, forms caustic soda by double decomposition:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

In many cases carbonate of soda is bought by the consumers, and made into a caustic lye by treatment with milk of lime.

The caustic soda lye thus obtained, concentrated to a given strength, forms the liquid caustic soda of commerce.

For the manufacture of solid $NaOH$ the lye is evaporated, until it solidifies on cooling, and is then ladled into iron drums to cool and solidify, and sent into the market at various degrees of strength.

A special brand of caustic soda has been introduced in commerce in the last few years—the powdered caustic soda of the Greenbank Alkali Co. It is found especially useful where no large quantities are used, and is invaluable for laboratory work. It comes generally in the form of white powder or very small lumps, sealed in tins, or in casks, and one quality is guaranteed to contain 98 per cent. of $NaOH$.

Carbonate of Potash (K_2CO_3) is now seldom employed in cotton bleaching, having been completely supplanted by the cheaper soda. It is, however, still used for special purposes, as it reacts in the scouring process in a less severe manner than soda ash.

The potash of commerce is the product obtained by the evaporation to dryness of the lyes produced in the lixiviation of the ashes of different plants, and is generally met in the form of white, bluish, or more or less tinged powders, varying considerably in the amount of K_2CO_3. It is also produced by a process similiar to Leblanc's soda manufacture.

As it is hygroscopic it is always well, in examining potash or pearl ash samples, to estimate the amount of moisture contained. The available agent in the commercial potashes is the K_2CO_3, and has to be estimated.

Caustic Potash ($K\,OH$) is seldom met with in commerce, although pretty largely produced, as it enters into the manufacture of soft or potash soaps. It is generally obtained by treating the lyes obtained by lixiviating the ashes of wood or plants, and then decomposing the solution by lime. It is now also brought into commerce in the dry state, being produced on a large scale.

ACIDS.

Sulphuric Acid ($H_2\,SO_4$) is generally bought concentrated of 66° Be′ or 170° Tw. 1·845 sp. gr. It is produced on an enormous scale by the old and well known process of lead chambers, mostly by means of pyrites, instead of sulphur, as formerly.

The first stage of the reaction is SO_2 or sulphurous acid gas, which is brought into the chambers when in connection with steam, air, and nitric acid vapours, and converted into sulphuric acid.

$$\underset{\text{Sulphur}}{S} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Sulphurous acid}}{SO_2}$$

$$SO_2 + O + H_2O = H_2SO_4$$

The product of the chambers, or the chamber acid, is used for many purposes if procurable at a short distance; but as a rule it is brought into commerce of the concentration of about 66° Be′ or 170° Tw.

When commercially pure it is colourless, or very slightly tinged, and is a very heavy, thick, oily liquor. Great care must be taken in handling the carboys containing sulphuric acid, and in getting the acid out of them, as many accidents are caused by carelessness in the handling and emptying of the carboys.

In Europe the acid carboys are enclosed in a wicker basket, or at most in an iron hooped basket filled with straw, but the Americans have a more practical method of enclosing the carboy in a wooden box. In this way they can be sent long distances with less danger of breakage, as only the top of the neck of the carboy is outside the box.

Sulphuric acid should always be tested for the specific gravity or degree of Twaddle or Beaume, as it is always so tested in the manufactory before sent out.

Hydrochloric Acid (HCl) (also called muriatic or marine acid, and spirit of salts) is obtained on a very large scale as a bye-product, in the manufacture of the sulphate of soda and soda ash by Leblanc's process. It is also largely produced in the Hargreaves' sulphate of soda process. By the latter method sulphurous acid gas is introduced in a series of large iron receivers, on the model of Wolf's bottles, filled with common salt, previously made into small blocks or balls by a special process.

By aid of heat, superheated steam and oxygen from the air, which is introduced along with the SO_2 gas, the chloride of sodium is decomposed and converted into sulphate of soda, while muriatic acid is evolved

$$2NaCl + SO_2 + H_2O + O = Na_2SO_4 + 2HCl.$$

the hydrochloric acid gas being absorbed in water in large stone towers constructed for the purpose, and brought into commerce in the same way as that obtained by the older process of decomposition of the NaCl with sulphuric acid.

Commercial hydrochloric acid is generally of a yellowish brown colour, due to chloride of iron or organic impurities, and shows generally about 30 to 33° Tw., or 1·175 sp. gr. It is generally bought at a given degree of the Twaddle hydrometer, and is consequently tested by the same.

BLEACHING POWDER

Is manufactured on a very large scale by the reaction of chlorine gas on slacked lime in specially constructed lead chambers. The commercial product forms a white powder, having a very strong smell of chlorine. When freshly prepared it has the empirical formula :—

$$Ca_3H_6O_6Cl_4.$$

If treated with water it is decomposed according to the following reaction :—

$$Ca_3H_6O_6Cl_4 = Ca(OH)_2 + CaCl_2 + Ca\,(OCl)_2 + 2H_2O$$

when the calcium hydrate remains undissolved, while the calcium chloride, $CaCl_2$, and the hypochlorite, $Ca(OCl)_2$ remain in solution ; the latter is probably only formed when the powder is treated with water.

It is the hypochlorite, $Ca\,(O\,Cl)_2$, which by its power of oxidation acts in bleaching by oxidizing, and destroying the colouring matters contained in the cotton fibre, consequently the value of a bleaching powder depends upon the amount of hypochlorite, or, as is generally stated, the amount of available chlorine, it contains.

Not only the bleaching powder is found in commerce but also the so-called bleaching liquor, which is a more or less concentrated solution obtained from ordinary bleaching powder by treatment with water.

If the liquor can be bought at a low price it is more convenient for use, especially in small works, than the powder, as it simply requires diluting with water to the required strength, while the bleaching powder must be treated with water before use.

Bleaching powder, or liquor, must be tested for the amount of available chlorine they contain. The strongest bleaching powder contains 38.5 per cent. available chlorine, but the commercial article varies from 32 to 37 per cent.

Some commercial bleaching liquors contain about 8 per cent of available chlorine. Several methods are recommended for estimating the commercial value of bleaching powders or liquors.

Among the different methods the following will be found useful :—

It relies on the oxidation of arsenious acid into arsenic acid—

$$As_2O_3 + Ca(OCl)_2 = As_2O_5 + CaCl_2.$$

A standard solution of $\frac{1}{10}$ normal arsenious acid is prepared by dissolving :—

4·95 grammes pure sublimed arsenious acid (As_2O_3) and
25 grs. recrystallized sodium carbonate in
200 cc. water,

the whole is boiled by shaking the flask repeatedly until dissolved, and then made up to

1 litre solution

which is kept in a well stoppered bottle for use. 1 litre of this $\frac{1}{10}$ normal solution corresponds to 3·546 grs. chlorine, while 1 cc. will correspond to ·003546 grs. available chlorine.

In conducting tests by this method a specially prepared paper is used which serves as indicator, and is obtained by moistening ordinary filtering paper with the following preparation :—

3 grs. starch are well mixed with 200 cc. water, with a wooden spatula, until the lumps are all broken up, the whole is boiled, then 1 gr. of iodide of potassium and 1 gr. of pure carbonate of soda are added, both previously and separately dissolved in a little water, enough water is then added to make up 500 cc. in all. The filter paper, saturated with this starch and iodide of potassium solution, is then dried, and can be kept in a well stoppered bottle for use.

TESTING OF BLEACHING POWDER.

Weigh 10 grammes commercial bleaching powder, place in mortar, add about 50 cc. cold water, stir well with pestle for several minutes and leave to settle. Pour liquor in a litre flask through a glass funnel. Treat residue in mortar again with water, leave to settle and pour again in litre flask, repeat until all the powder has been washed into the litre flask. Add cold water up to the litre mark and shake well.

Take 50 cc. of this turbid solution and place in a glass beaker, then add from a burette $\frac{1}{10}$ normal arsenious acid solution, until a drop of the liquor applied on the starch iodine paper no longer forms a blue spot. Some chemists make the test on the filtered liquor instead of using the turbid solution.

This reaction is due to the iodine, which is liberated by the chlorine, and made to react on the starch to give its well known blue colour.

The number of cc., found on the arsenious acid solution, multiplied by ·003546, will give the amount of available chlorine contained in 50 cc. of the bleaching powder solution, and consequently ½ gramme of bleaching powder, from which the amount contained in 100 can be easily calculated.

Bleaching liquor is tested in the same way:—

100 grs. or cubic centimeters of the solution are diluted to 1 litre with water, the amount of chlorine estimated in 50 or 100cc., and then calculated for percentage.

TESTING ACIDS AND ALKALIES.

When buying acids the usual and only test generally employed is the estimation of the Twaddle or Beaumé degree, or the specific gravity, as, although this is not always a certain guide, it is pretty reliable for such acids as sulphuric or hydrochloric. It should, however, be borne in mind that the specific gravity, and consequently the degree, varies to a certain extent, according to the temperature, and therefore it is advisable to make this test always at a given temperature of 15° C, by immersing a glass full of the acid in a vessel containing water at about that temperature, and allowing it to stay there until the acid itself shows 15° C. This practice, however, is seldom followed on account of the trouble it involves; but it would not be difficult to arrange a table of the variation of the degree Tw. according to the degree of temperature.

In the process of bleaching, the weak acids and liquors are also tested by means of the Twaddle, but this test is not always a reliable one; for instance, when preparing a fresh acid solution the degree of Tw. will give a fair indication of the amount of acid, but if, as very often is the case, the acid liquors are used several times, it will be found that the liquor, although showing the same degree of Tw. as before, will not contain the same amount of acid. For instance, the souring liquor, which remains after liming and washing, or even after bleaching, will contain a certain amount of lime salt, which accumulates in the acid liquor according to the number of times it has been used, and increases the degree of Twaddle. It is best in bleachworks not to rely implicitly on the employment of the Tw., but on the more certain plan of chemical estimation by volumetric analysis.

THE MINERAL COLOURS.

Although the mineral colours are not so largely employed as formerly, they still form an important class, and some are indispensable to the modern dyer or calico printer.

They are fixed on cotton in two ways; as ready made *Pigments*, by the aid of a fixing medium, such as albumen, &c., or by applying first the mordant and afterwards developing the colour in another bath.

Among the pigments the white products form a very important group, not so much for printing purposes, where only a limited application is found, as in producing white patterns on coloured cotton goods, but some of them are largely employed in finishing processes.

WHITE PIGMENTS.

Chalk or Whiting ($CaCO_3$) is found in nature very extensively, and is pretty largely employed in dyeing or printing for dunging purposes, for the fixation of mordants, &c.

It is also used, to a certain extent, in finishing, as a filling material, and as an adulterant or reducer of some pigment colours.

For dunging purposes it should be free from iron or iron impurities, and for finishing, a good colour and great fineness, with absence of grit, are indispensable.

Gypsum *(Sulphate of Lime)* is solely employed for filling or finishing purposes, and only to a moderate extent.

Zinc White *(Oxide of Zinc)* (ZnO.) is sometimes employed in printing for mixing with coloured pigments.

The commercial product, which is obtained by the combustion of zinc in air, or by calcination of precipitated basic zinc-carbonate, is sometimes also used for printing white designs on coloured ground.

Barium Sulphate ($BaSO_4$) *(Permanent White)* is seldom used in finishing cotton goods, but the product is principally used as an adulterant for ultramarine and other pigments, owing to its great specific weight.

The ground natural product has not so much covering power as that obtained by precipitation.

It is very often produced, as a bye-product, in the preparation of mordants, such as sulpho-cyanide of alumina, and in this form is employed generally as a resist paste, for which it acts mechanically.

China Clay *(Silicate of Alumina)*.—Very largely used for finishing purposes and weighting. It is found in nature in large quantities, and is the product of desintegration of felspar. It is produced very largely in Cornwall.

The commercial article varies considerably in quality and therefore in price; if used for white or light coloured goods it should be of as good a white as possible, in a fine state of division, and thoroughly free from grit or sand. China clay contains about 11½ per cent. of water. In estimating commercial samples the whiteness and fineness of the product are the characteristics by which a judgment is formed.

YELLOW PIGMENTS.

Chrome Yellow ($PbCrO_4$). — Chromate of lead, or yellow chrome, is largely used by the calico printer in the form of a pigment, and is found in commerce of different strength and shade, generally in paste form and ready for printing. It is manufactured by precipitation of a soluble lead salt by means of bichromate of potash or soda, also by treating the sulphate of lead, which is obtained as a bye-product in the manufacture of acetate of alumina, by means of bichromate of potash. The commercial product may be tested by estimating the amount of water it contains, and the colouring power must be estimated by printing in comparison with a standard sample.

Chrome yellow is dyed pretty largely on cotton cloth, and is also produced on prints by printing a thickened colour containing acetate or nitrate of lead, and then developing the colour, or as it is termed, raising the yellow, in a bath of bichromate of potash.

Chrome yellow is a fast colour, but has the great drawback of blackening when exposed to sulphuretted hydrogen. It is still, however, very largely employed in dyeing and printing, as it is the only really fast, and at the same time cheap, yellow at our disposal.

Commercial chrome yellows are often mixed with white pigments, such as barium sulphate, &c.

Chrome Orange. — When neutral chromate of lead is treated with lime water, it is converted into a basic chromate, which turns towards orange and red according to its basicity.

The commercial chrome orange pigments are mixtures of chrome yellow and the red basic chromate (Pb_2CrO_5)., being obtained by treatment with lime. Like chrome yellow, it is bought by the calico printer in the form of paste, and in estimating its commercial value the amount of dry pigment must be determined, and its colouring power tested by a practical printing trial.

Chrome orange is also very often produced on the fibre by dyeing or printing; a strong chrome yellow being produced which is rendered basic, and consequently converted into orange, by passage through a hot bath containing milk of lime or lime water.

Cadmium Yellow (*Sulphuret of Cadmium*) would be very useful for dyeing, and especially so for printing, if it was not so expensive. The advantage it possesses over the lead yellow is that it does not become black when exposed to sulphur-fumes, or sulphuretted hydrogen. It is found in commerce as a pigment ready for printing, but is very often produced in the printworks. The method of developing this yellow by a direct printing process will be found described in the practical recipes.

Of the other yellow pigments only one or two are employed, and then in special cases only, for instance :

CHROMATE OF BARIUM ($BaCrO_4$).—This is neither as fast nor as brilliant a colour as chromate of lead, over which it has only the advantage of not blackening when exposed to sulphuretted hydrogen.

ZINC CHROMATE, or the basic chromate of zinc, is also a yellow pigment, which is seldom used. It cannot be compared in fastness against soaping with lead chromate, but it possesses over the latter the same advantage as the barium salt towards sulphuretted hydrogen.

BUFF (French : *chamois*).—Oxide of iron is also reckoned among the yellow colours, though it scarcely belongs to them ; the commercial product comes generally in the form of paste, like all the other pigments, and is largely used for producing very light grounds. Buff shades are produced by dyeing and printing in several ways, all aiming at precipitating the oxide, or rather the hydroxide, on the fibre. The production of buff colours by printing will be found among the other recipes.

CANARIN *(Persulphocyanogen Yellow)* ($C_3N_3S_3H$). —Although known a long time it is only lately that this product has attracted the attention of chemists, and has been utilised as a colouring matter, for which it possesses the advantage of great fastness against light, acids, soap and bleaching liquor. It is brought into commerce as a ready-made dyestuff under the name of *canarin*, being combined with potash or borax, and can in this state be employed as a steam colour, or fixed directly on the fibre by oxidation, by a method similar to that used for aniline black. Canarin is an oxidised product of sulpho-cyanides; the oxidation being effected and canarin produced by treating potassium or any other sulpho-cyanide, by means of a chlorate and sulphuric or hydrochloric acid. The yellow can also be formed by oxidation of any sulphocyanide by means of arsenic acid on the water bath.

METALLIC POWDERS.

Metallic powders are used for some special purposes in calico printing to produce metallic effects; they are generally either silver or gold powders, very seldom, however, of the genuine precious metals, but mostly alloys, manufactured principally in the town of Nürnberg, in Germany.

The bronze powders, which when printed have a golden appearance, are generally alloys of copper, zinc, or tin, and are first of all beaten into leaves, which are then pressed through metallic sieves by means of stiff brushes, and thus made into a fine powder.

But different from these bronze powders is the

Argentin or Argentan, which is simply tin precipitated in a fine state of division, and is prepared in the following way:—

In an earthenware vessel capable of holding 10 litres or 2 to 3 gallons, a solution of zinc chloride is placed of 18° Tw., 5 oz. or 100 grammes of tin crystals are added, and the whole stirred until dissolved; strips of zinc are then immersed in the solution, and left in until no more tin precipitates down, when the whole is passed through a silk sieve, and the precipitated tin, after washing well with water, is dried in a moderately heated stove, and forms the so-called argentin of commerce.

It is fixed on calico by printing with ammoniacal caseine, and the cloth is afterwards passed through a heavy calender, and hot pressed; a metallic lustre is acquired by the metallic powder, which was originally without brightness.

The metallic powders, generally, are printed on by means of gum, or fixed by albumen. Another method consists in mixing bronze powder with a silicate of soda solution, and printing without any other thickening than that effected by the silicate solution.

The drawback connected with the employment of these metallic powders is that they very often fill the engraving of the printing rollers.

RED PIGMENTS.

Cinnabar or Vermilion.—Sulphide of mercury is still used in calico printing, but has lost much of its importance since the production of fine reds by means of alizarin.

The commercial product, which, if pure, gives a fine bright shade, is very often adulterated with less valuable reds, which impair the beauty of the colours.

An imitation of vermilion, the spurious vermilion or *vermilionette,* which has been for some time in use in painting, is nothing but red-lead coloured with eosine.

In order to detect adulteration in vermilion, a thorough chemical analysis is necessary.

A practical trial may be made by printing with egg albumen.

Of the other red pigments there is no application in printing, or their employment is too limited to call here for any useful remark.

GREEN PIGMENTS.

The green pigments can be divided into two classes. The first comprises mixtures of blues and yellows, such as Prussian blue and chrome yellow, and the second, those colouring matters which are of definite chemical constitution, as chrome green.

The mixed greens are produced in great variety, but although largely employed in painting, they have no great importance in calico printing.

Guignet or Chrome Green.—This is a very important pigment colour, and is in fact the oxide of chromium. It is produced on a large scale by more than one process, one being the treatment of bichromate of potash with boracic acid. Three parts boracic acid and one part bichromate of potash are heated together in a furnace, after being made into a thick paste with water, and brought to a dull red heat. After cooling, the mass is thrown into water, the borate of chromium is decomposed, and $Cr_2O_3 + 3H_2O$ settles down as a fine green powder, which, after washing and draining is brought into commerce either in the wet state as a paste, or dried and sold as powder.

Good and fast shades of green are produced by this pigment, which, although not so bright as other greens such as arsenite or acetate-arsenite of copper, has, however, the great advantage of not being poisonous, and must therefore be preferred. A practical printing trial is the only reliable test for the commercial estimation of this colouring matter. There are several other methods by means of which chrome green pigments can be produced, among which is the treatment of bichromate of potash with phosphates, and it is probable that some of these reactions might be utilised for the production of mineral green in direct printing by the preparing of steam colours. For instance, it is very likely that in the formation of the phosphate of chromium, green is due to the reduction first of all of chromic acid to chromic oxide, which then combines with phosphoric acid to form phosphate of chromium. There would not be any difficulty in preparing a colour containing bichromate of soda and a soluble phosphate, and a reducing agent, which would act in the steaming of the cloth to reduce the chromic acid to the oxide, and thus allow the combination to take place on the fibre.

POISONOUS GREENS.—*Scheele's green*, or arsenite of copper, and *Schweinfürt green*, or acetate-arsenite of copper, give bright shades, but ought never to be employed in calico printing, owing to their poisonous character, since they can never be so fixed on calico as not to be liable to dust off, and therefore there is always danger of poisoning by inhaling the dust shaken from the prints.

The employment of these poisonous greens, although now of rare occurrence in calico printing, ought to be given up altogether.

BLUE PIGMENTS.

ULTRAMARINE.—This is an important pigment, and is used very extensively, not only for printing but for tinting purposes, giving that pleasing blue tinge to cotton, either after the process of bleaching or in the finishing operations. Originally the precious stone *lapis lazuli* was ground to powder and employed in painting, its price being very high; and the merit of having produced ultramarine falls to Guimet and Gmeling, who, independently of each other, devised methods for its artificial manufacture. The discovery of ultramarine is one of the most important events in the history of modern chemistry, and like many other scientific discoveries, it has been brought about by the labours and observations of several chemists.

Guimet started the manufacture of ultramarine in Lyons, in 1827, and the sale price was originally 600 francs the kilo, which, however, was speedily reduced.

Ultramarine is still manufactured in France, but not so largely as in Germany. England has, as yet, not taken a very prominent share in the production of this useful pigment, although the largest producer of China clay or caolin, which is the most important raw material in its manufacture. Ultramarine is produced in two distinct stages: –

1st.—The preparation of green ultramarine.

2nd.—Conversion into blue.

For the first operation the mixture of caolin, charcoal, and sodium sulphate or soda, after being well ground together is ignited in a suitable furnace, when a white mass is produced, which becomes green by exposure to air. The conversion into blue is then effected by calcination in contact with air, by roasting the green product with sulphur at a low temperature. There are several modifications of the processes, as there are three general methods for the manufacture, according as the soda, sulphate, or silica ultramarines are required. The conduct of this manufacture requires attention and practical skill. In commerce there are many varieties of ultramarine, distinguished by four principal qualities:—

1st.—Deep pure blue.
2nd—Pale blue.
3rd.—Ultramarines with violet hue.
4th.—Ultramarines with dull greenish hue.

In testing samples of ultramarine, as of all dry pigments, a comparison with a standard sample is generally resorted to. Both samples are placed on a piece of white paper and the shade judged by pressing one of the samples down by means of a flat piece of glass, or by means of paper on which the hand is laid, and then putting in the middle of the flattened sample a small amount of the other sample and flattening again, when the difference will be strikingly apparent. By this means difference in either strength or shade can be at once detected. Commercial ultramarines are generally largely adulterated with white pigments, principally barium sulphate, and it is therefore a question of importance to be able to estimate the strength of commercial samples. This is done, of course, by comparison with a standard sample; the stronger sample is mixed or diluted with sulphate of barium until it shows the same strength as the other, the ultramarine and the barium-sulphate having been weighed before mixing will at once indicate the ratio of strength of the two samples. Ultramarine must be in a fine state of division, and quite free from grit, and a simple test consists in dropping a small pinch of the sample into a glass tumbler or cylinder full of water, and, after agitating, to see the time it takes in settling, the finer the powder the longer it remains in suspension. But the most reliable test is by printing and fixing by means of albumen, and steaming. Some varieties of ultramarine, though of a lighter shade, are more expensive than others of a darker hue ; this is due to the greater degree of brightness or purity of colour possessed by the former; consequently the proper discrimination of ultramarines requires great experience, since chemical analysis is useless for the purpose, the more so that the constitution of the composition of ultramarines has not yet been established.

The colours produced by ultramarine in printing are absolutely fast against air and light, and when properly fixed with albumen stand soaping well.

Ultramarine is rather sensitive against acids, for instance, it is decomposed by hydrochloric acid, and is even affected by strong vinegar ; some varieties will not even stand alum.

The natural product, while resisting the action of strong vinegar and alum thoroughly well, is also decomposed by hydrochloric acid.

Quite recently methods have been studied for producing ultramarine by a cold process.

PRUSSIATE BLUES.

These have lost much of their former importance since the introduction of coal tar colours. Of the cyanogen colours the most important is *Prussian Blue.*—This colour was discovered in 1710 by Diesbach, but Scheele proved at the end of last century the relationship between Berlin blue and yellow Prussiate.

The discoveries of Prussian blue and of artificial ultramarine have had a very important bearing in tinctorial arts and the chemistry of colours, and may be considered the first steps in the series of brilliant discoveries in colour chemistry, and its industrial application, during the present century.

Yellow Prussiate of Potash (*Ferro cyanide of Potassium*) ($K_4FeCy_6 + 3H_2O$.) is manufactured on a large scale, but is not so important a product as formerly, the employment of prussiate blues, of which it forms the principal raw material, having greatly decreased, owing to the introduction of the blue aniline colours. Although more direct processes have been recommended and tried on a large scale, the older principle is still followed in the yellow prussiate manufacture, viz: that of igniting mixtures of carbonate of potash with organic residues containing nitrogen, such as horn, leather residues, blood, wool residues, &c., and iron filings, and afterwards lixiviating the mass with water.

The product is generally found in commerce in large yellow crystals of quadratic prisms, soluble in three to four parts of water, of which it contains about 12 per cent. It forms coloured precipitates with many metallic oxides; the one with Ferric oxide, Prussian blue, being the most important. A solution of Ferric salt will give Prussian blue, if mixed with a solution of yellow prussiate, while a ferrous salt produces a white or very pale blue precipitate which, if oxidised by long exposure to air, or by rapid oxidation with nitric acid or chlorine is converted into Prussian blue. Recently the prussiates have been recommended for the fixation of aniline colours in calico printing. Yellow prussiate reacts as a reducing agent; and prussiate of soda is an article of recent introduction into commerce.

Red Prussiate of Potash *(Ferricyanide of potassium)* (K_3FeCy_6).—This is also an article of commerce, produced in only limited quantities by the reaction of chlorine gas on a solution of yellow prussiate.

$$K_4FeCy_6 + Cl = KCl + K_3FeCy_6$$

It forms ruby red crystals, which react as a very powerful oxidiser, and is in fact utilized for this property of oxidation in several printing processes, as, for instance, in discharging indigo blues in connection with caustic alkalies, &c.

$$2K_3FeCy_6 + 2KOH = 2K_4FeCy_6 + H_2O + O$$

A solution of red prussiate gives with proto salts of iron a blue precipitate called *Turnbull's Blue*, which, if not identical with Prussian blue, is very similar to it. In both the yellow and red prussiates the potash only acts in binding the cyanhydric acid iron compound, which in the free state can be illustrated by the formulæ:

H_4FeCy_6 Ferrocyanhydric acid
H_3FCy_6 Ferri ,, ,,

the hydrogen being capable of displacement by metals.

Prussian or Berlin Blue (Fe_7Cy_{18}) is obtained by treating solutions of yellow prussiate with ferric salts, for instance,

$$3K_4FeCy_2 + 2Fe_2Cl_6 = 12KCl + Fe_7Cy_{18}$$

It may be considered as a combination of the ferrous and ferric cyanide—

$$3FeCy_2 + 2Fe_2Cy_6 = Fe_7Cy_{18}.$$

The commercial product, which is known under different names, such as Chinese blue, Prussian or Berlin blue, &c., is a mixture of the neutral and the basic prussiate blue, more or less adulterated with other pigments.

The Neutral Blue is produced by pouring a solution of ferro cyanide of potassium into one of a ferric salt, principally ferric chloride or sulphate; the precipitate is afterwards washed and dried, but always retains a certain amount of yellow prussiate, which water cannot remove.

The Basic is obtained by first precipitating a solution of a ferrous salt, such as copperas, with yellow prussiate, and then oxidizing the white precipitate, the ultimate product being partly soluble in water, or in the prussiate of potash solution used in excess. As a pigment, Prussian blue is scarcely ever used in printing, but often in finishing certain kinds of cotton goods, to which it imparts a coppery appearance. Of late it has been extensively employed in finishing black cotton velvets, to which it gives that blueish hue pecular to the so-called Linden blacks. In this case it is employed as an oil colour mixed with linseed oil or varnish.

In printing, the employment of prussiates is still important in some special styles. The blue is formed by direct processes, and developed on the fibre. Important properties of Prussian blue are the solubility in oxalic acid solution, and the decomposition which takes place when treated with alkalies, such as caustic soda, which destroys Prussian blue by forming ferric hydrate and ferro prussiate of soda.

Prussian blue is improved considerably in shade if a certain amount of tin is introduced in the colour. This is fully illustrated in the preparation of printing colours.

BROWN PIGMENTS.

Although there is a great variety of mineral brown pigments, very few of them are employed in calico printing. They are generally found in commerce in the form of ready made pastes under different names, such as pigment brown, chocolate, &c., and are mixtures of different products, in some cases simply minerals, very finely ground, the shade being modified by the addition of other coloured pigments.

The Ochres are found plentifully in nature, being mostly composed of oxide or hydroxide of iron, more or less mixed with chalk or clay.

The yellow ochres which are distinguished from the red by their shade, are often used for finishing purposes, simply mixed in the size.

Light buff colours are very often produced on calico as padded ground on a coloured design, by padding a very light ochre colour with albumen, and then fixing by steaming,

In commerce there are also the burnt ochre colours, the shades of which are more intense or darker than the others, metallic pigments of deep brown colour containing manganese.

Burnt sesquioxide of iron, which is obtained as a bye-product in some chemical processes, is of a violet brown colour, going up to dark red in its finest shades. But all these mineral products are of only limited interest to the calico printer, who has now at his disposal such a variety of products which give browns in great variety at a low price and of fast shades.

MANGANESE BROWNS will be mentioned later on, as they are produced on the fibre.

BLACK AND GREYS.

As a black pigment the only one largely employed is LAMP BLACK, which is carbon in a very fine state of division. In commerce prepared paste colours are sold under different names, which are simply pulverised charcoal or lampblack, sometimes modified in shade by means of a logwood black lake. But these black pastes have lost their former importance, and are now only sparingly used.

By dilution these blacks yield grey shades which, as in the case of the black, are fixed by means of albumen, and are of absolute fastness to air and light. They can be modified very greatly in shade by the addition of ultramarine or other pigments.

On the whole, pigments are not very largely used in calico printing, as the pigment styles have not been popular during the last few years. By mixing pigments, olives and many other compound shades are produced.

NATURAL ORGANIC COLOURING MATTERS.

LOGWOOD

Is the wood of a tree of the order of *Leguminosœ,* a native of South America and the West Indies, and known botanically as *Hœmatoxylon Campechianum,* of which there are several varieties, distinguished by the names of the places where they are grown, such as Spanish logwood, Mexican, St. Domingo, Honduras, Campechy, Laguna, &c.

This dyewood is generally found in commerce in the form of logs, hence its name, but is supplied to the customers either rasped or chipped, or in fine powder, or as extract.

The colouring matter contained in this wood is found as a glucoside. The wood is very often exposed to a kind of fermentation or oxidation by wetting the ground or chipped material with water, and allowing it to stand for a certain time in order to decompose the glucoside, when

HÆMATOXYLIN is obtained; this is not a colouring matter *per se,* but must be oxidized into the HŒMATEIN, as by the formula:—

$$\underset{\text{Hæmatoxylin.}}{C_{16}H_{14}O_6} + O = \underset{\text{Hæmatein.}}{C_{16}H_{12}O_6} + H_2O$$

which is the true colouring principle of this dyewood, and which forms differently coloured lakes with different metallic oxides; the most important of which being those produced with iron and chromium mordants.

Besides the colouring matter, logwood contains a certain amount of tannic acid, which, of course, plays an important part in the fixation of some colours.

The extract obtained from logwood will never be found to contain hæmatein only, but may still contain the glucoside, and in many instances the larger proportion of the dyestuff, still in the form of hæmatoxylin, and a certain amount of tannic acid also.

Logwood and its commercial extract are very largely used in dyeing, principally for the production of blacks, the formation of a great variety of greys, and compound colours, such as browns, olives, &c.

It is very largely employed in calico printing, mostly for blacks or very deep blues, and many combinations of colour.

The colouring matter of this wood is very soluble, especially in hot water. It gives the following coloured lakes with the metallic oxides :—

With Alumina	Purple shades.
,, Copper	Deep indigo blue to black.
,, Ferrous Oxide	Bluish black.
,, Ferric ,,	Brownish black. Ferrous and ferric oxides combined, best blacks.
,, Chromates and chromium mordants.	Blacks becoming greenish by exposure.

A peculiar reaction of the colouring matter of logwood is, when in solution in water, if treated with acids it turns red.

This reaction is very often utilized as a test for dyed goods, which are supposed to be dyed or topped with logwood, by placing a small bit in water acidulated with sulphuric or hydrochloric acid ; if the piece contains logwood it will be shown at once by the red colouration it imparts to the water.

Logwood Extract comes in commerce of different strengths, mostly of about 40° to 50° Tw. in a syrupy form or as a dry extract.

Hæmatine.—Under this name in the last few years a product has been introduced in commerce which is the colouring matter of logwood in a very pure form ; when price allows it can be employed in the same way as other logwood preparations.

The Testing of the commercial value of logwood and extracts can only be effected by practical trials of dyeing and printing.

The extracts of logwood are sometimes largely adulterated with chestnut extract, and this adulteration is rather difficult to detect by chemical analysis, but will be shown by the practical trial; the iron black obtained with such an adulterated logwood extract is of a browner shade, and the chrome blacks will come out poorer than if pure logwood is used, since the chestnut extract does not fix well on chromium mordants, and does not give even such fast shades as logwood.

Sometimes the logwood extract is adulterated with a small amount of impure magenta, but seldom with other aniline colours, which can be easily detected by dyeing a sample on unmordanted wool.

Special Logwood Preparations.—In the last few years special products have been introduced in printing, either for the production of blacks, or deep indigo-like blues; they are derivatives of chromium combinations, and some of them yield very good results. They will be mentioned again later on.

RED WOODS.

These are divided into two classes:

1st—Those, the colouring matter of which is easily soluble in water, such as peachwood, Brazil wood, sapan, Lima wood, &c.

2nd.—Those possessing the dyestuff not readily soluble in water, such as barwood, camwood, &c.

The red woods have sunk considerably in importance since the introduction of coal tar colours.

Red Woods with Soluble Colouring Matter belong to the class *Cæsalpina*, and seem to contain the same colouring principle. The Brazil, Lima and peachwood are produced in South and Central America, while sapan is brought into commerce from India, Japan and China.

The colouring matter is found in the wood in the form of glucoside, which, when decomposed, produces a sugar, and a product called *brasilin*, $C_{22}H_{20}O_7$.

The red dyewoods are not largely used as self colours, but principally in combination with other dyestuffs for the production of compound shades, both in dyeing and in calico printing (especially in the steam styles), when they are generally connected with mordants and a certain amount of chlorate; with alumina mordants blueish reds are produced, while with iron and alumina browns and chrome, brown up to chocolate shades. The commercial extracts generally show 40° to 50° Tw.

They are principally employed for the preparation of red lakes, for paper staining, painting, &c.

Of the other class of red woods, barwood and camwood are now used, in diminishing quantity, in cotton dyeing, but never in direct printing. Barwood was at one time used, and is yet to a small extent, for the production of colours on cotton cloth, which imitate, pretty well, the old turkey-reds.

BARWOOD comes from the tree *Baphia Niterda,* growing in Sierra Leone.

RED SANDERS or Santal Wood is a native of India, the small tree *Ptecarpus santalinus,* and contains the colouring matter *Santalin.*

MADDER.

The pulverised root of *Rubia tinctorum,* which at one time was one of the most important dyewares, has been now completely displaced by artificial alizarin. It is still employed to a certain extent in wool dyeing.

GARANCINE, the derivative of madder, is now seldom used in the garancine styles in calico printing, and in cotton dyeing it has been completely given up.

COCHINEAL

Is another natural organic dyestuff which has suffered by the introduction of coal tar colours. In printing it is still used, but its employment is decidedly on the decline. Although up to a few years ago a very important colouring matter, it has been little studied by chemists, and has been only lately fully investigated by Liebermann.

Cochineal is formed by the bodies of small insects (*Coccus cacti*), which are cultivated in Mexico and Central America, the Canaries, &c., the insect living on a species of *cactus* (*opuntia*), and only the female possessing dyeing properties.

The commercial product is distinguished as *white* or silver grey, which is the insect before laying eggs, and *black*, which is the body of the female insect after the eggs have been laid. Adulteration is practised very largely in this product, the white being mixed very often with sulphate of barium to the extent of 12 to 23 per cent., and the black is adulterated with the material after the colouring matter has been extracted, which is then dried and mixed with the genuine article; another form of adulteration being granulated lead. In some cases white cochineal is actually produced by colouring black cochineal with a white pigment.

The colouring matter of cochineal is stated to be CARMINIC ACID ($C_{17}H_{18}O_{10}$) (?), and forms coloured lakes with metallic oxides, of which those with alumina and tin are the most important.

COCHINEAL CARMINE has a certain resemblance to the turkey-red lake, as it contains a large amount of alumina and lime, combined with a nitrogenous matter, which seems to answer to the oily matter of the turkey-red lake. Its manufacture is still kept a trade secret.

A commercial sample examined by Liebermann gave the following analysis ;—

Water	17	per cent.
Nitrogenous matter	20	,,
Ash	7	,,
Colouring matter	56	,,

The ash of the carmine containing—

Alumina	43·	per cent.
Lime	44·8	,,

According to Horace Koechlin, cochineal contains two distinct colouring matters; the smaller quantity produces the carmine with alumina, and the other gives red precipitates with tin salts, and violet reds with alumina.

YELLOW DYESTUFFS.

QUERCITRON BARK.—This is a dyestuff still largely used in the printing and dyeing of cotton goods. It is the bark of a variety of oak, *Quercus tinctoria,* growing abundantly in some parts of the United States, particularly Pennsylvania.

The colouring matter is found in the form of a glucoside called *Quercitrin,* which can be split up into a kind of sugar and *Quercetin* ($C_{27}H_{28}O_{12}$), which is the colouring principle forming coloured lakes with metallic oxides. Quercitron is found in commerce in the form of bark, powdered or not, and largely in the form of extracts, principally liquid extracts, which have the tendency to easily ferment, and which very often by long standing deposit crystals of the pure colouring matter. An estimation of the colouring power is made by practical trial of dyeing or printing.

Quercitron is largely used in printing, being found especially useful in compound colours. Owing to the tendency of quercitron extracts to crystallize out of solution, it is advisable, in order to ensure even shades, to agitate well the contents of the cask before use, or to heat the extract until the crystals are redissolved.

FLAVINE is a very pure, dry extract of the colouring matter of quercitron bark, prepared by a process not generally known. It yields purer shades than the bark or the extract, and when price is not an objection is preferable to either.

PERSIAN BERRIES

Are a very useful product for the calico printer, since they yield an extract which is very largely used in the production of steam yellows and other compound shades. The berries, which are about the size of small peas, are the fruit of the *Ramnus infectoria.* The colouring matter is found here also in the form of a glucoside, which in splitting up yields *Rhamnetin* ($C_{12}H_{10}O_5$), which behaves in a similar manner to quercetin, but is superior to the latter in the beauty of yellows it produces in printing, which are a little faster than those obtained by means of quercitron.

Of Persian berries there exist in commerce liquid extracts, and a carmine or lake, which are found very useful by the calico printer. As extract it enters very largely in producing compound steam colours of great variety.

FUSTIC

Is not a very important dyewood for the calico printer, and its most important application is in the dyeing of blacks on mordanted cloth, and other compound colours with logwood, for which, however, it is largely substituted by bark or quercitron.

It is the wood of the *Morus tinctoria*, which comes from South America, and the West Indies. In commerce it is met with both in the log, rasped, chipped, or ground, or as extract. The colouring matter is formed by two substances—*Moritannic* acid ($C_{13}H_{16}O_6$) and *Morin* ($C_{12}H_8O_5$).

The yellows, or straw colours produced with fustic on cotton are not very bright, stand light fairly well, but do not stand soaping.

TURMERIC

Is only sparingly used now, principally for cotton yarn dyeing. The colouring matter is *Curcumin* ($C_{10}H_{11}O_3$), which is insoluble in cold, but sparingly soluble in hot water.

There are several other yellow colouring matters, but they are little if at all employed by the calico printer, and therefore need not be mentioned here.

ANNATTO

Is still used in plain dyeing and in printing to some extent. It gives light salmon up to orange shades, which are produced with very great facility. It possesses only a moderate degree of fastness, although sometimes used with fast shades. The commercial product, which is very seldom met with pure, is obtained from the seeds of the tree *Bixa orellana*, a native of South America.

The colouring matter of annatto is *bixin*, which is an acid giving soluble combinations with alkalies, on which property is founded its employment in dyeing and printing. Annatto contains another colouring product called *orellin*, which is, however, of less importance. In dyeing it is employed in a carbonate of soda solution. In printing it is better dissolved in caustic soda and methylated spirit.

In testing commercial samples of annatto, the amount of ash will give an indication of its purity, a fair commercial sample giving about 20 per cent. ash. Powdered brick forms one of the chief adulterants, and plaster of Paris, starch, &c., are also very often used for the purpose.

The microscope will be found useful in detecting many organic adulterations of annatto.

CUTCH OR CATECHU

Is one of the most important dyestuffs employed by the cotton dyer, and is at same time a valuable product in calico printing, because it yields shades of absolute fastness to light and soap.

It is not only employed as a self colour for the production of browns, but is very extensively used, in combination with other dyestuffs, to produce compound colours of great variety, such as drabs, greys, olives, dark browns, chocolates, &c.

The commercial products are the dry extracts obtained from several Indian trees, species of *Acacia, Areca, Butea, Uncaria,* &c., and are generally found in commerce either in the form of small cubes, or of large lumps or cakes, in boxes.

The colouring matter is the catechin, *Catechuic Acid* ($C_{13} H_{12} O_5$), which is soluble in water, acetic acid, and weak alkalies.

Catechuic, or as is also called catechutannic acid, forms very stable compounds with metallic oxides, producing coloured pigments principally of brown or bronze shades; for instance, with copper salts fast bronze colours are obtained, with protochloride of tin a brownish yellow, with tin perchloride and copper a deep bronze, with alumina reddish brown, with iron greys of different hues and strength almost up to black, &c.

Of these coloured lakes or pigments, the most important are produced by means of bichromates or by chromium mordants, and an oxidizer, along with catechu extract, in direct printing, being browns of great fastness.

Commercial catechu contains always a certain amount of tannic acid, which can be separated from the catechuic acid by digesting with cold water, in which the latter is scarcely soluble, while the former goes in solution.

Cutch is very often classed as a tanning material, and is used in some cases as such, as in cotton black dyeing.

The testing of catechu is effected by a practical trial, either by dyeing or printing, or the tannic acid may be estimated by volumetric analysis.

A quick, and at the same time pretty accurate method is to extract a weighed sample with ether, and after the ether has been driven off to weigh the tannic obtained. Good qualities of cutch contain from 40 to 52 per cent tannin.

Among the commercial varieties of catechu may be mentioned the brown varieties, which comprise—

PEGU CATECHU in cakes of 30 to 40 lbs. packed in leaves.

Brown Cutch, in cubic cakes, coming from Java and Singapore.

Bengal Cutch, in small cubic blocks.

Gambir or Gambier, a yellow variety obtained from the leaves of *Uncarta Gambier*, is also known as cubical cutch, and is found in commerce in the form of thick flat cakes.

ALOES

Give, under certain conditions, shades which have been at one time utilised for either dyeing or printing, but only to a moderate extent. The employment of aloes in printing is limited to the production of brown shades of great fastness and peculiar hue, which have the drawback of coming out uneven.

INDIGO.

If not the most important of dyestuffs, indigo is a product of the highest importance in the dyeing and printing of cotton, for which it possesses the most valuable of all qualities for tinctorial application—great fastness. It was one of the earliest products employed in the colouring of fabrics, and is probably one which has given rise to calico printing.

Indigo is the derivative of plants of the family of *Papilionacœ,* of different species of *Indigofera,* which grow in India, China, the West Indies, South America, and Africa, the most important being the *Indigofera-tinctoria,* and *Argentea disperma,* the plants reaching a height of three to five feet. Like many other natural organic dyestuffs, the colouring matter is not found ready formed in the plant, but is in a state of glucoside, called *Indican* by Schunck, which when exposed to fermentation is split up into a peculiar kind of sugar called indiglucin, and

Indigotin, or the pure colouring matter of indigo, and is illustrated by the following equation :—

$$\underset{\text{Indican.}}{C_{52}H_{62}N_2O_{34}} + 4H_2O = \underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_3} + \underset{\text{Indiglucin.}}{6C_6H_{10}O_6}$$

The manufacture of indigo, although improved to a certain extent in the last few years is still conducted, in a very primitive manner, and it would be worth while to study the question with the idea of improving the production; not only by increasing the yield, but by introducing into commerce a product possessing a known and regular amount of indigotin.

The colouring matter is found principally in the leaves, but for the production of indigo the young plants, or the branches, twigs and leaves, are worked up. They are treated with water in tanks sometimes by the aid of a little lime or ammonia, and exposed to a kind of maceration and fermentation which lasts from 9 to 12 hours. The liquor is then run off into tanks at a lower level, where by strong agitation the indigotin is gradually formed, and is afterwards allowed to settle, separated from the liquor and boiled in caldrons in order to prevent any further fermentation taking place, which would destroy the colouring matter.

After filtering and pressing, the product is dried, and is ready for the market, where it is sent principally in the form of cakes, packed in boxes or in chests.

No doubt this is the cheapest method which could be employed, but it is a question, after the indican has been extracted from the plants or leaves, with water containing a small amount of sulphurous acid or a bisulphite, in order to prevent fermentation, if a larger yield could not be obtained by decomposing the indican by means of weak sulphuric acid (as was at one time done in the case of madder for producing garancine), and utilise at the same time the sugar solution for producing alcohol by fermentation. The quality of commercial indigo varies considerably in the amount of indigotin it contains, some samples containing 80 or 85 per cent., some only 20 and even 15 per cent., the latter, of course, being adulterated.

INDIGOTIN ($C_{16}H_{10}N_2O_2$) has the following characteristics: It possesses a deep blue colour, is insoluble in water, is not attacked by weak solutions of acids or alkalis, and is indifferent to soap; hence its utility as a fast colour.

A very valuable property of indigotin, which is utilised for its fixation on the fabrics, is that it can be converted by reduction into *Indigo white,* and is then rendered soluble in weak alkaline liquors; the reaction is illustrated by the following equation:—

$$\underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + H_2 = \underset{\text{Indigo White.}}{C_{16}H_{12}N_2O_2}$$

If a fibrous material is immersed in a bath of reduced indigo white in alkaline solution, it takes up the indigo white solution, which by exposure to air is reoxidised to indigo blue, and therefore rendered insoluble and permanently fixed on the fibre.

$$\underset{\text{Indigo White.}}{C_{16}H_{12}N_2O_2} + O = H_2O + \underset{\text{Indigo Blue.}}{C_{16}H_{10}N_2O_2}$$

This is the theory of the employment of indigo in dyeing, and the reduced indigo bath is generally called the *Vat.* There exist several methods of reduction which will be mentioned in the practical part. They can be divided into two classes, utilising

1st.—The fermentation and organic reducers.

2nd.—Reduction by means of metallic compounds.

Indigotin by oxidation is converted into a colourless body, or into a product possessing no tinctorial power, and called *Isatin*; and on this reaction relies the process of discharging indigo dyed goods.

$$\underset{\text{Indigotin.}}{C_{16}H_{10}N_2O_2} + O_2 = \underset{\text{Isatin.}}{C_{16}H_{10}N_2O_4}$$

The blue is destroyed where the oxidising discharge has been applied, a white pattern being produced on blue ground. By addition of suitable ingredients to the discharging colour, coloured discharges or patterns can be obtained on blue ground by the process which will be explained later on.

Indigo is very often accompanied by *Indigo red* or *Indigo rubin,* a purple colouring matter which plays a pretty important part in the dyeing process, as it imparts to goods that reddish or purple hue characteristic of some brands of indigoes. It possesses a similar property to indigotin, being capable of reduction, and consequently of becoming soluble in alkaline liquors.

WOAD *(French pastel)* is a dyestuff obtained from *isatis tinctoria,* and was in use in Europe before indigo was introduced. It is now employed in the preparation of the fermentation vat along with indigo, but not in very large quantity. The colouring matter possesses the same characteristics as indigotin, to which it has many points of resemblance, if it is not identical.

ESTIMATION OF COMMERCIAL SAMPLES OF INDIGO.—There are many methods recommended for estimating the amount of indigotin in commercial samples, mostly relying on the employment of volumetric analysis; but all the methods, if very useful in the hands of skilled chemists, cannot be considered as thoroughly satisfactory, as they only deal with indigotin, and do not take into account the organic impurities accompanying it. Although some of the chemical methods are useful, principally as comparative tests, only practical tests by dyeing are thoroughly reliable. Even these, if not carefully conducted, are liable to error.

The following method of estimation of indigotin has been recommended by Mr. C. Rawson, in a paper read last year before the Society of Dyers and Colourists in Bradford, and the following table containing his results of the valuation of Indigoes, by the different methods, will show at once how different percentages are obtained from the same samples by the different methods of estimation:—

One gram of finely powdered indigo is ground into a thin paste with water, and introduced into a flask with 500 to 600cc. of lime water. The flask is furnished with an india-rubber stopper, which has four perforations, in one of which is inserted a syphon closed by a pinchcock, and in another is fixed a funnel provided with a stopcock; the other two apertures serve for the entrance and exit of a current of coal-gas. The flask is connected with a supply of coal-gas, and the contents heated to about 80° C.; 100 to 150cc. of a solution of sodium hydrosulphite are now introduced by means of a funnel, and the mixture, which in a few minutes takes a yellow tint, is kept near the boiling point for half an hour. After allowing the insoluble matters in the flask to subside, 500cc. are syphoned off, and the remaining liquid accurately measured.

The 500cc. are poured into a conical flask, and by means of an aspirator a current of air is drawn through the liquid for about twenty minutes. The excess of hyposulphite is thus oxidized to sulphite, and the indigo-white to indigo-blue. When hydrochloric acid is added to sodium hyposulphite, a copious precipitate of sulphur occurs, but after oxidising the liquid by a current of air, the solution remains perfectly clear on the addition of an acid. An excess of hydrochloric acid is therefore added in order to dissolve any carbonate of lime which the precipitate may contain. The precipitate is collected upon a weighed filter, thoroughly washed with hot water, dried at 100° and weighed. The weight thus obtained is indigotin and indigo-red. If it is desirable to determine the amount of each of these constituents, the filter with its contents is placed in an extraction apparatus, and the indigo-red dissolved out by means of alcohol.

Example.—One gram of indigo is reduced by a mixture of sodium hyposulphite and lime-water. The liquid measured 935cc. 500cc. are oxidised, and treated as above described. Weight of precipitate = ·243;

$$\therefore \quad \frac{\cdot 243 \times 935 \times 100}{500 \times 1} = 45{\cdot}44\,^{0}/_{0} \text{ indigotin and indigo-red.}$$

The filter is placed in the extraction apparatus, and the red dissolved by means of alcohol. The alcohol solution is evaporated to dryness, dried at 100° and weighed. Weight of extract = ·015. From this amount one miligram is subtracted in order to allow for the slight solubility of indigotin in alcohol.

$$\therefore \quad \frac{\cdot 0135 \times 100 \times 935}{500} = 2{\cdot}52\,^{0}/_{0} \text{ indigo-red.}$$

Indigotin (by difference) = 42·92 $^{0}/_{0}$

The principle of this method can be applied to a volumetric process, by means of which, in given samples of indigoes, concordant results can be obtained in less than half-an-hour. But the impurities of indigoes are somewhat affected by the reaction.

Table Showing the Percentage of Indigotin in various Classes of Indigoes, by the Employment of Different Methods of Analysis.

METHOD.	I. Java.			II. Bengal *a*			III. Bengal *b*			IV. Oude.			V. Kurpah.			VI. Madras.		
	Highest	Lowest	Mean	Highest	Lowest	Mean	Highest	Lowest	Mean	Highest	Lowest	Mean	Highest	Lowest	Mean	Highest	Lowest	Mean
1. Permanganate (direct)	76·32	76·05	76·18	66·76	66·68	66·71	62·85	62·32	62·60	50·22	49·86	50·04	47·15	47·15	47·15	39·92	39·30	39·50
2. Permanganate (after Precipitation by Sodium Chloride)	73·82	73·27	73·55	...	...	63·50	57·74	57·30	57·50	..	...	44·90	43·30	42·90	43·10	...	...	37·40
3. Hyposulphate (Volumetric)...—	68·92	68·05	68·78	59·52	58·86	59·20	55·84	55·21	55·60	43·28	43·08	43·18	42·72	42·32	42·52	37·35	36·56	36·80
4. Sublimation	61·03	60·69	60·84	57·95	57·12	57·50	50·50	48·22	49·36	41·96	41·25	41·60	42·37	41·48	41·92	40·42	38·52	39·56
5. Reduction (by Ferrous-sulphate and Sodium Hydrate)	68·50	67·82	68·24	59·43	58·12	58·84	56·03	53·59	54·34	...	...	41·50	41·75	40·88	41·50	34·95	33·88	34·50
6. Reduction :— (Hyposulphite and Lime)																		
Indigotin	69·25	68·65	68·97	59·35	58·89	59·12	56·64	55·92	56·20	43·65	42·99	43·42	42·79	42·15	42·68	35·42	34·98	35·21
Indigo Red	4·50	4·01	4·23	3·84	3·24	3·50	3·00	2·60	2·80	3·93	3·42	3·65	2·52	2·25	2·45	4·12	3·75	3·98
Percentage of Water	...	...	2·99	5·28	5·15	5·22	6·25	6·10	6·17	...	...	7·50	...	...	8·05	5·80	5·62	5·71
„ Ash	...	...	1·99	...	...	3·91	...	...	4·86	...	...	8·21	25·85	25·62	25·72	33·75	33 50	33·62

MANUFACTURE OF EXTRACTS.

The production of dyewood extracts has in the last few years developed into a large manufacture. The principal extracts are the following:—*Logwood, Fustic, Quercitron* or bark, *Red wood* extracts, comprising sapan, peachwood, lima, &c., and *Persian berry.*

The extracts of tanning materials, such as Sumach, Galls, Chesnut extract, &c., are also largely produced, but the latter belong more to the mordants, and will be treated later on. In the manufacture of dyewood extracts the principle followed is theoretically a very simple one—the extraction of the colouring matter by treatment with water, and the evaporation of the latter in order to obtain the extract in a syrupy or dry state. But the business of extract making is a much more complicated one than is generally supposed. First of all, in importance, is the selection of the dyewoods. This requires a practical knowledge of the commercial varieties and their approximate corresponding colouring power. The dyewoods are subjected to the mechanical process of disintegration, by breaking or cutting up the material into small pieces, in order to allow the water to penetrate, and extract the colouring principle. The selection of a good machine for rasping or chipping the dyewood is also of primary importance to the success of extract making, as the colouring matter is generally found in dyewoods, as a glucoside. The splitting up of this for obtaining the free colouring matter has not received the amount of attention from the majority of wood extractors that the process deserves. For instance, in the case of logwood, a kind of fermentation is resorted to before the extraction is proceeded with, and although at first glance this appears the cheapest process, the question should be considered whether the decomposition of the glucoside could not be affected by other means, as weak sulphuric acid, and the sugar thus liberated utilised? The process of extraction by water is also a very important one, the problem being the extraction of the maximum quantity of colouring

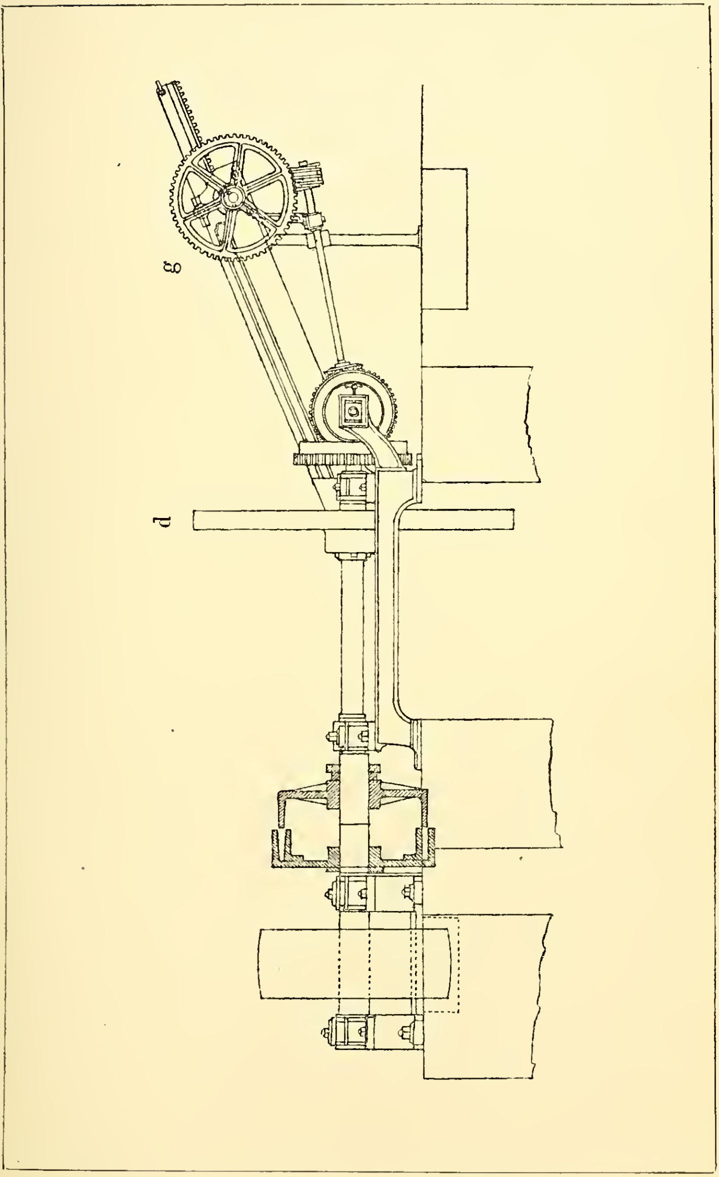


Fig. 1.—RASPING AND CHIPPING MACHINE.

matter with the minimum quantity of water. The practice of extracting varies considerably in different works. In large dyeworks and some printworks the extractors employed are simply horizontal boilers with double bottoms, in which the disintegrated wood is introduced and the extraction performed by means of water heated by direct steam, the pressure reaching in some cases 20 lbs., or even higher. The extractors are generally constructed of iron, but sometimes made of copper, the latter in some cases being preferable.

There are several kinds of machines for the cutting or rasping of dyewoods, one of which is shown by the accompanying diagram (Fig. 1.) The machine consists of a stout iron disk (*d*) revolving at high speed on its axis. On the disk is a series of knives, which are fixed through holes pierced in the disk itself, and so arranged that they project a little from the surface of the disk, and the log of wood, being pushed by a special guiding arrangement (*g*) against the disk, in a perpendicular line, is cut into chips. By changing the form and construction of the knives different qualities of product can be obtained, varying from coarse chips to pretty fine powder and sometimes splinters.* Sometimes along with this rasping or chipping machine is connected a grinding machine, also called a disintegrator, (Fig. 2) which converts the wood into very fine powder. This machine is mainly composed of four arms revolving at high speed round their common axis, and which effect the grinding of the wood against the teeth, as shown in the illustration, the whole being closed by means of a cover. In some works the extraction is performed at as low a temperature as possible, not higher than 60 or 70°, even cold water is used in the diffusion process. In these instances either wooden vats or cemented vessels can be used, the extraction with hot water being effected by the water going

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*I must here acknowledge my thanks to Messrs. Schofield & Sons, for allowing me to inspect, and to make some trials with the machine, which was originally designed by Mr. W. Barker, and will, no doubt, be found useful for other purposes where a cutting or chipping up of wood is necessary.

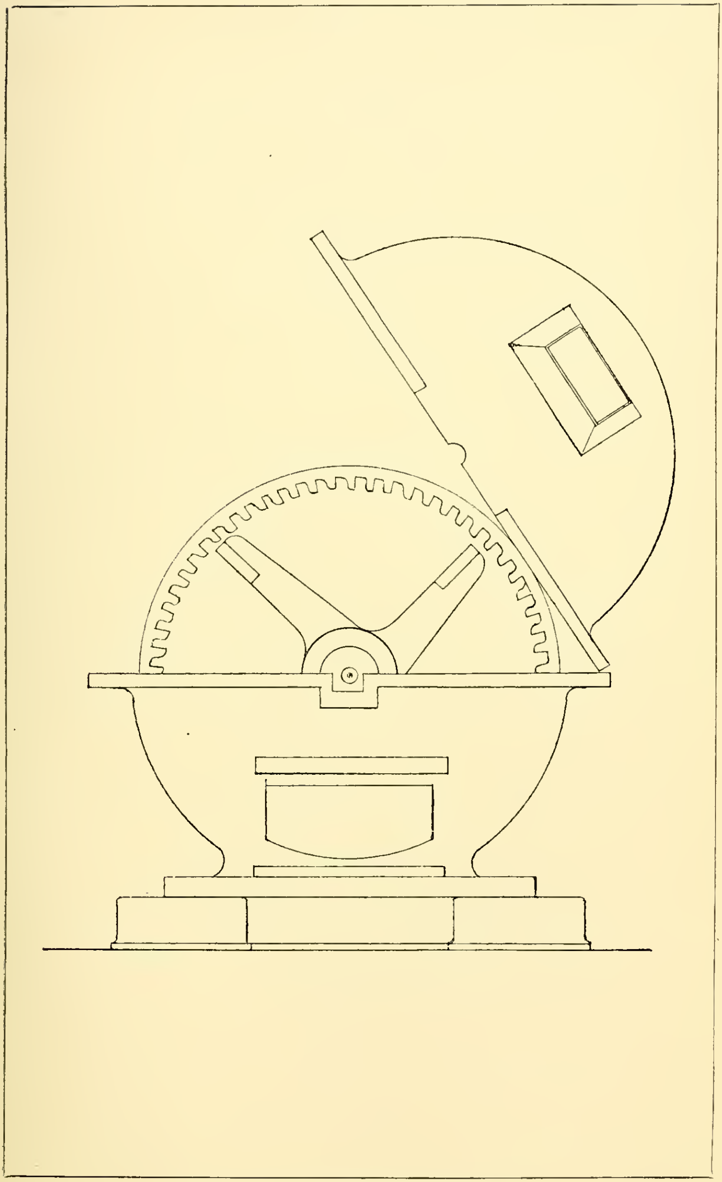


Fig. 2.—DISINTEGRATOR.

from one vat into another until the liquor is obtained as concentrated as possible; while at the same time, the wood is left completely exhausted. More time is required by this system, but the extract obtained is in many cases of purer quality than that obtained by extractors working under pressure. The quality of the water plays a more important part in extracting dyewoods than is generally believed; for instance, the excellence of some brands of fustic extracts of French manufacture are, to a great extent, due to the quality of the water in the neighbourhood of Paris, as well as to the methods of extraction and evaporation. The question of the evaporation of extracts is also of very great importance. As a rule, the evaporation ought to be conducted at as low a temperature as possible. The apparatus employed for the evaporation are various, and a great deal of the success of the manufacture of extracts depends on the employment of suitable apparatus.

For several years an apparatus has been employed in France, to which must be ascribed in a great measure the success of some French dyewood extract makers. This apparatus or evaporating machine, if properly constructed, is the most convenient and most economical evaporator in use. It was invented by Chenailler, and is made on the best principle on which an evaporator could be constructed—that of exposing the evaporating liquor to the action of agitation on a very large surface in a thin layer. Fig. 3, for which I am indebted to Messrs. Bonsor and Co., of Bradford, illustrates the principle of the apparatus. The machine consists of a concave cistern containing the liquor, through which revolve, at slow speed, a set of double convex chambers heated by low pressure steam. The chambers are all fixed round a hollow axis of special arrangement, through which steam is introduced on one side, while the condensed water is let out at the other extremity.

The revolving chambers are supplied with buckets or cups fixed on the sides, which in going through the liquor take up a certain quantity, and spread it over the heated surface in a thin layer, which considerably hastens the

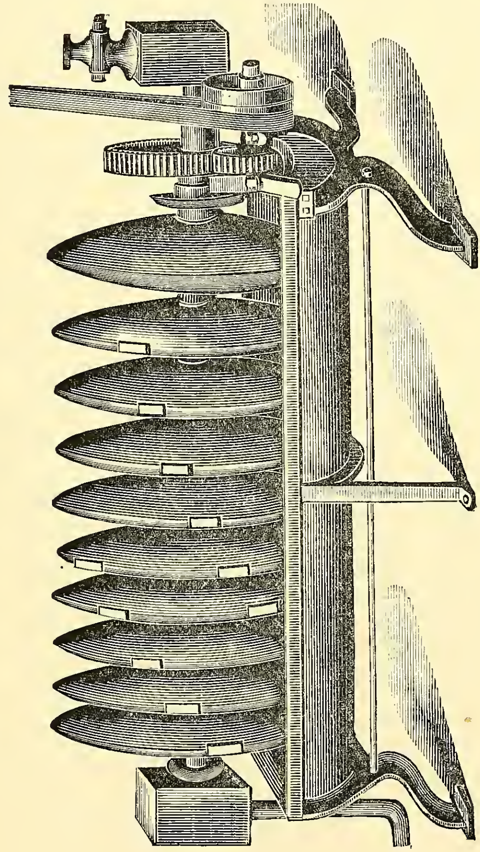


Fig. 3.—CHENAILLER'S EVAPORATOR.

evaporation. These machines, when well constructed, are very economical in their work, since they can be worked with the exhaust steam of a high-pressure engine. According to the temperature and quantity of the steam introduced into the evaporating chambers; the temperature of the evaporation can be regulated as low as 70° C., or higher if necessary.

One of the above machines, which are generally constructed of copper, will evaporate over 850 gallons in 24 hours.

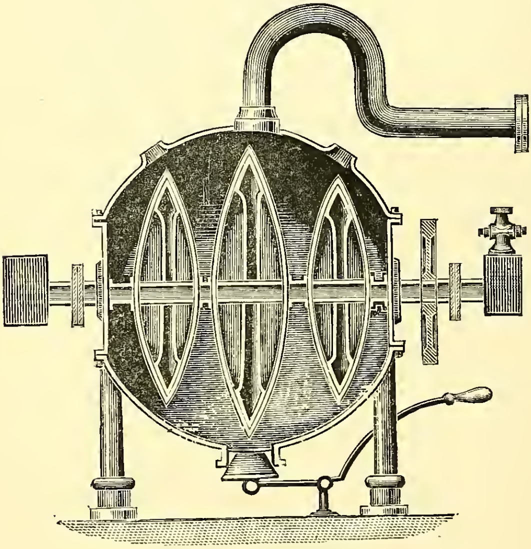


Fig. 4

As a rule the evaporation is conducted in this apparatus up to a certain point, when the extract is brought into a vacuum apparatus, similar to those used in sugar works, where the evaporation is continued. Fig. 4 illustrates a modification of this machine, and shows the section of three chambers; in this case, the apparatus is supplied with a cover in order to conduct the steam out of the building by means of a pipe connected with a chimney, blower, or vacuum pump, and thus combining the principles of evaporation on a large surface by aid of agitation, and in connection with vacuum. Liquid extracts are generally produced in these apparatus, while dry extracts are manufactured on flat iron evaporators with double bottoms, heated by steam, and supplied with mechanical agitators, on which the extracts are evaporated to a certain consistency, and then run into boxes for facility of carriage. Both liquid and dry extracts are very often adulterated with glucose, sugar, dextrine, &c.

LAKES.

Lakes are the precipitates formed by organic colouring matters with metallic oxides. They can be obtained in very great variety, any organic dyestuff being capable of yielding lakes of different shade and colour, according to the metallic compound employed; but these products have lost their importance since the development of steam colours in printing. Some of the lakes are yet employed and fixed on calico by means of albumen, but their principal use is in paper staining, for which purpose they are largely employed.

There are in commerce black lakes which are derivatives of logwood, either precipitates with iron or chromium compounds, sometimes mixed with lamp-black.

Madder lake, also called rose lake, the alumina compound obtained from madder, is now seldom used in calico printing, since reds and pinks can be so easily produced by direct printing with alizarin. The lake of the Persian berry extract, or as it is called Persian berry carmine, which is a tin derivative, is still largely used in printworks. The cochineal carmine lake, which is an alumina derivative, is still of some importance, owing to the fine shades it produces when printed with albumen. Of the other lakes few are employed, and those only for special purposes, and these could, without much loss, be replaced by other dyestuffs or direct printing processes.

As a rule lakes can be produced as follows:—The dye-stuff is extracted by water, and mixed with a solution of a metallic salt, alum or sulphate of alumina being mostly employed, and the lake precipitated by means of an alkali and afterwards filtered and washed, and generally brought into commerce in paste form.

COAL TAR COLOURS.

Coal Tar, which is obtained as a bye-product in the manufacture of gas, is carefully collected and treated by the tar distiller, who separates it into several products, among which the most important may be mentioned :—

Carbolic Acid.
The Benzols or Benzenes.
Naphthaline.
Anthracene, &c.,

which are of utility in the manufacture of coal tar colours.

The colouring matters obtained from coal tar are consequently divided into three classes, viz :—

The *Benzol colours,* which comprise all the aniline dyes, and also the carbolic acid or phenol dyestuffs.

The *Naphthaline* colours which comprise the azo products.

The *Anthracene* derivatives, principally alizarin, &c.

THE BENZOL COLOURS:

PRINCIPALLY ANILINE COLOURS.

The benzol products of coal tar consist of hydrocarbons, and are generally a mixture of different constituents or homologues, benzol, toluol, xylol, &c. As these compounds show different boiling points they can be separated from each other by fractional distillation, and on a large scale by means of an apparatus called Coupier's column. These hydrocarbons have the following formulæ, from which will be seen the different chemical reactions they have to go through before converted into colouring matter.

Benzol or Benzene.	Toluol or Toluene.	Xylol or Xylene.
C_6H_6	C_7H_8	C_8H_{10}

These compounds have the property of being converted into nitro products when treated by mixtures of concentrated nitric and sulphuric acids, and the products obtained are

Nitro Benzol.	Nitro Toluol.	Nitro Xylol.
$C_6H_5NO_2$	$C_7H_7NO_2$	$C_7H_9NO_2$

The following equation for benzol will illustrate the reaction that takes place.

$$C_6H_6 + HNO_3 = H_2O + C_6H_5NO_2$$

These nitro products by reduction are converted into the corresponding amines or amido products.

$$C_6H_5NO_2 + 6H = 2H_2O + C_6H_5NH_2$$

Aniline	Tuluidin	Xylidin
$C_6H_5NH_2$	$C_7H_7NH_2$	$C_8H_9NH_2$
Amido Benzol.	Amido Toluol.	Amido Xylol.

These amido products, which are simply bases belonging to the ammonia class, can be converted by oxidation, &c., into colouring matters of great variety. We shall here mention only those which have found extensive employment in dyeing and printing.

ANILIN.

Anilin is manufactured on a very large scale by the reduction of nitro benzol by means of iron filings and hydrochloric acid. There are different varieties of anilin in the market, distinguished from each other by their boiling points, which vary as the benzol used in the manufacture of the nitro-product is pure C_6H_6, or mixedwith toluol or xylol; the resulting anilins will have different adaptabilities for the production of colouring matter, or for employment in dyeing and printing, being either pure anilin or a mixture of this with toluidin and xylidin. Anilin comes in commerce either as aniline oil, or, combined with hydrochloric acid, as aniline salt.

PURE ANILIN.—$C_6H_5NH_2$ is an oily liquid, colourless when freshly distilled, but becoming brown by standing. It is a powerful base, and forms salt with acids, some being well crystallised. Boiling point: 182°C. This quality of aniline is best adapted for the manufacture of fine aniline blues from rosanilin, as will be seen later on. The way to test aniline and commercial aniline oil generally is—

1st. By dissolving a sample in weak hydrochloric acid in a beaker or glass, when it must go completely in solution.

2nd. By the boiling point, as follows:—In a small glass retort provided with a stopper, through which is passed a thermometer held in its place by means of a cork, place 200cc. aniline oil: see that the bulb of the thermometer lies in the liquid, and heat carefully on a bunsen burner. The retort is connected with a condenser, and the distillate is allowed to drop into a graduated 100cc. glass cylinder. The temperature is noted when the aniline begins to distil over, and the temperature is also noted at which every 5 or 10cc. come over.

A third method is a practical trial to test the aniline oil for the purpose for which it is intended, either dyeing, printing, or colour-making.

The aniline manufacturers have by long experience found out the best quality of aniline for the different purposes, and they consequently bring into commerce different brands under the following names —

Aniline for blue.
,, for red.
,, for black dyeing.
,, for printing.

Aniline Salt ($C_6H_5NH_2HCl$).—Hydrochlorate of aniline is also very largely manufactured and brought into commerce either in the form of crystals or as a fine powder. It is only employed for cotton dyeing or for calico printing, and is manufactured accordingly for the purpose. It is tested: 1st—By decomposing 10 to 50 grammes of the salt in solution in hot water by means of caustic soda, and then adding common salt enough to make a saturated solution, when the aniline oil collects at the top of the water and can be measured. If this test is made in a flask or bottle with neck graduated in cc, or even in a graduated glass cylinder, it can be read off at once. By decomposing a larger quantity of the aniline salt, the aniline oil obtained can be tested for the boiling point in the manner previously described.

2nd. By titrating with normal alkaline solution.

The principal employment of aniline salt in printing is in the production of aniline black, a colour of great fastness. It is sometimes also employed for producing a black lake, either alone or in connection with logwood, the lake being fixed by means of albumen, but it is little used in this form.

It is in all cases advisable to test the aniline salt for the purpose for which it is intended, either by dyeing or by printing.

PHENYLEN DIAMINE $C_6H_4(NH)_2$.—Many trials have been made to utilise this product in calico printing for the production of fast brown shades by oxidation, with little success. Binitro benzol when treated with a reducing agent is converted into phenylen diamine

$$C_6H_4(NO_2)_2 + H_{12} = C_6H_4(NH_2)_2 + 4H_2O,$$

and is very largely produced in the manufacture of Bismarck brown, the product employed for printing being simply the liquor of phenylen diamine hydrochlorate evaporated to dryness on the water bath. It produces, by oxidation in printing, shades varying from light drabs to deep, bronze browns, which are distinguished by great fastness.

NAPHTYLAMIN ($C_{10}H_7NH_2$) is obtained by reduction of nitro naphthalin.

$$C_{10}H_7NO_2 + H_6 = C_{10}H_7NH_2 + 2H_2O,$$

of which the modification *alpha* has been principally employed in printing, but not very extensively. It forms the raw material for the manufacture of several azo colours.

DIMETHYL ANILINE ($C_6H_5N(CH_3)_2$.) is produced on a large scale, and serves as raw material for methyl violets, the greens, methylene blue, &c. It is a product of the reaction of methyl alcohol and hydrochloric acid on aniline. The attempt has been made to utilise this base in printing by oxidation in the same way as aniline black, but it only yields a grey, which, although very fast, is of scarcely any practical utility.

MAGENTA ($C_{20}H_{19}N_3HCl$.).

The hydrochlorate of rosanilin is produced on a very large scale by two methods, one relying on the employment of arsenic acid, the other on the treatment of nitro benzol and aniline in presence of hydrochloric acid and iron filings, as by Coupier's process. Magenta has declined considerably in importance since the introduction of other red colouring matters derived from coal tar. The magenta base or rosanilin ($C_{20}H_{19}N_3OH$) combines with acids to form well defined salts. The product employed in commerce is mostly the hydrochlorate, and is principally in crystallised form. The acetate is often found in commerce; it is more expensive than the hydrochlorate, but is generally purer and more readily soluble in water. It yields stronger solutions of the colouring matter, which can be kept a long time even in the cold, especially if a small amount of methylated spirit is added in dissolving. The magenta crystals are principally employed in dyeing; while the acetate (also used in dyeing) can be employed more advantageously in printing. This colouring matter was at one time largely employed as a raw material for the production of other aniline colours, but is now only used for the preparation of the aniline blues. The crystals of the hydrochlorate are soluble in hot water or alcohol, but they are not very soluble in cold water. This dyestuff is now seldom used as a self colour in printing, owing to its want of solidity against light and soap, but it is extensively used in compound shades. In dyeing it is principally fixed in tannic acid or mordant; in printing, either with albumen or by tannic acid, in the same way as the other aniline colours.

THE ANILINE BLUES.

These dyestuffs are produced from rosanilin or magenta base, and are found in commerce in great variety of shade and strength.

The products insoluble in water, but soluble in spirit, are phenylated rosanilins; the greener shade, or what is generally called opal blue, is a *Triphenyl rosanilin*

$$C_{20}H_{16}(C_6H_5)_3N_3HCl$$

generally combined with hydrochloric acid. Less phenylated compounds are of a redder hue. They are generally produced by the action of aniline or rosanilin and acid, either acetic or benzoic acid, when the phenylisation takes place with the evolution of ammonia, thus:—

$$\underset{\text{Rosanilin.}}{C_{20}H_{19}N_3} + \underset{\text{Aniline}}{3C_6H_5NH_2} = C_{20}H_{16}(C_6H_5)_3N_3 + 3NH_3$$

The triphenyl rosanilin comes in commerce in the form of dry powder, sometimes consisting of very fine crystals, and if employed for cotton dyeing it must be dissolved in spirit before use at the rate of about 4 oz. of colour per gallon of hot alcohol, or 2½ per cent.

There are also solutions of this colouring matter in commerce produced by means of the acetate, which is more soluble in alchol, the solution even keeping in the cold.

The mono and diphenyl rosanilins are also found in the market under different names, generally containing more or less of the three phenylated compounds, and according to the proportion of each, the shade varies from a reddish to a greenish hue. The mono phenyl product is the reddest, being more a violet than a blue dyestuff.

These insoluble compounds are also found in commerce as a paste, of which two shades are supplied; one green, the other red. Both are employed in calico printing, and fixed by means of arsenic, glycerine, and acetate of alumina. The paste of a green shade, which is obtained from the pure opal blue, or triphenyl rosanilin, is known as *Gentiana* or *Ceruline blue.*

The shades obtained both in dyeing and printing with the triphenyl rosanilin blues are brighter than those produced by any other aniline colours; and are as yet unrivalled.

Unfortunately, while the shades obtained in printing stand soaping pretty well, they are not fast against light.

The method of fixation of these opal blues on cotton by dyeing, consists in mordanting cotton with a 10% solution of Marseille soap, drying, and then dyeing in a bath of acetate of alumina at 1 to 2° Tw., to which is added sufficient of the opal blue solution in alcohol for the depth of shade required; the dyeing is started cold, and is heated gradually to boiling; the longer it boils the greener is the shade. Soap and lead acetate can also be employed for the mordant.

THE SOLUBLE BLUES.

These products are obtained from the phenylated rosanilin by treatment with sulphuric acid, which converts them into sulphonated compounds, soluble in water. These sulphonic acid derivatives, form the alkaline or Nicholson blues, which are the monosulphonic acid salts of soda, and are obtained by treating the insoluble blues with sulphuric acid, in a temperature not higher than 100° F. The monosulphonic acid thus produced is thrown into water, washed by decantation and filtration, and dissolved by means of carbonate or caustic soda in hot water, and evaporated to dryness or sold in solution. The di and tri and tetra sulphonic acids form the soluble blues, especially the cotton blues, which consist principally of tri and tetra sulphonic acid combined with soda or ammonia. The alkaline blues are used in silk dyeing and cotton printing, but their principal employment is in the dyeing of wools.

The soluble blues are employed to only a moderate extent in printing, while for cotton dyeing, those mostly used are the so-called cotton blues, which stand dyeing in a bath containing an addition of alum.

All these soluble blues, when applied on cotton, are very loose and do not stand soaping, therefore, they are never employed in fast styles.

DIPHENYL AMINE,

AND METHYL DIPHENYL AMINE BLUES.

These products are found in commerce either in the form of spirit or soluble blues, and are obtained by the oxidation of the corresponding bases. They are applied in dyeing by the same methods as those followed in the ordinary aniline blues.

METHYL VIOLETS.

These have displaced the older Hoffman's violets, and are manufactured on a very large scale, and found in commerce in great varieties of strength and shade, generally from 3 or 4 R to 6B.

The normal methyl violet is the penta methyl para rosanilin, having the formula

$$C_{19}H_{12}(CH_3)_5N_3HCl.$$

It is obtained by oxidation of dimethyl aniline, generally by employing sand or salt—a copper salt and a chlorate, the mass being made into cakes which, placed in shallow vessels, are exposed in stoves to slow oxidation for several days. The colouring matter is afterwards extracted by means of boiling water, salted out, and purified by dissolving and precipitating again with common salt; the shade obtained by this method is 2B, the redder shades are generally mixtures of violet with magenta, and the bluer shades are produced by treating the 2B product with benzyl chloride. More direct methods of producing these colours have been introduced in practice. They are very extensively employed in dyeing and printing, and are fixed principally by means of tannic acid, or corresponding products. These violets are very soluble in hot water, and to a certain extent even in cold water; they belong to the basic colours, being generally the hydrochloric acid salts of the violet bases, and may be considered as methylated, and to a certain extent, benzylated rosanilin.

These violets find extensive employment, both as self and as auxiliary colours, especially in printing, as in mixtures of violet and greens for deep blues, or of methylene blues and violet for deep indigo blue shades; these are often found ready mixed in commerce. Violet is also largely used for topping other colours, such as alizarin purples, indigo, blues, &c.

HOFFMAN'S VIOLETS

are seldom, if at all, manufactured now; those found in commerce under this name are simply methyl violets.

CRYSTAL VIOLET

Is a product recently introduced in practice, and is the HCl salt of hexamethyl pararosanilin, being obtained by a direct process from dimethyl aniline.

It is readily soluble in water, and gives a bluer shade than methyl violets.

METHYL GREEN

Is obtained from methyl violet, principally by the action of chloride of methyl.

This product, which is found in commerce either in crystalised form or in powder, has lost a considerable portion of its importance since the introduction of the Malachite greens, which being obtained by a direct process from dimethyl aniline, are much cheaper than the methyl greens. It is, however, still used, both in dyeing and calico printing.

The formula of methyl green is as follows:

$$C_{19}H_{12}(CH_3)_5N_3CH_3Cl.\ HCl.$$

being chlormethyl compound of the violets.

The commercial product is generally the double chloride of zinc and the green dyestuff. It is also a basic colouring matter, and is fixed with tannin. The shades obtained, especially in printing, are pretty fast against soaping, and are very often connected with aniline black.

Greens Derived from Dimethyl Aniline, by Direct Methods.—These products are known in commerce under different names, such as

Benzaldehyde green.
Malachite, solid, or
Fast green, benzoyl.
Victoria green, &c.

They are seen very often in the form of very fine crystals, or as powder, as a zinc double salt or oxalate. They have found extensive application, and have largely supplanted the methyl greens. They are mostly produced by the reaction of benzotrichloride, or benzaldehyde on dimethyl aniline, in presence of zinc-chloride; the leuco base, a colourless product, is first produced, which after precipitation and washing with water is dissolved in HCl. and oxidised. They are principally fixed by tannic acid. Instead of dimethyl aniline, sometimes the diethyl compound of aniline is employed, and the greens thus produced are of yellower tone than the former.

During the last few years several products have been introduced as acid greens, which are sulphonated compounds of these green dyestuffs: these, however, have no interest for cotton dyeing or printing, although very useful for wool and silk.

Of these commercial products the *Malachite green* is obtained from benzotrichloride and dimethyl aniline, and the zinc double salt has the formula

$$3.(C_{23}H_{24}N_2HCl.) + ZnCl_2 + 2H_2O.,$$

and is sold either in crystals or in powder.

For printing purposes either of these greens, of a basic character, can be employed, provided they yield good shades, the colouring power and price of the respective brands will be a basis for discriminating between them.

METHYLENE BLUE.

$$C_{16}H_{18}N_4S.HCl.$$

This is a very important product for cotton dyeing, and is one of the most useful blues at the disposal of the calico printer, since the shades produced from it vary from a light and bright blue to deep indigo.

The light blues, although very brilliant, are not to be compared with those produced by means of the opal blues or the prepared blue paste, although they possess the advantage of standing light much better.

The shades produced on cotton both by dyeing and printing with tannic acid stand soap fairly well, and methylene blue may be considered a fast colour, although not equal to indigo or alizarine in this respect.

This dyestuff is also a derivative of dimethyl aniline, which is first converted into the nitroso product, and then treated with sulphuretted hydrogen, and the product oxidised by means of ferric chloride into the methylene blue. This is separated from the solution by the addition of zinc chloride and common salt, being precipitated as a zinc double salt, and after drying is brought into commerce in the form of a powder. A method employing the electric current has been recommended lately for producing this dyestuff.

Methylene blue is applied on cotton by the ordinary method with tannic acid, the shades varying from fine light to deep colours according to the amount of dyestuff used.

It is interesting to observe that very light shades are very bright, but this brightness is lost when deep colours are dyed.

In calico printing methylene blue is largely used, not only as a self colour, but especially for light shades, which are exceedingly bright, but do not match those produced by means of opal aniline blues. In combination with violets it is also extensively employed for producing dark blues.

AETHYLENE BLUE

Is a similar product, and possesses almost the same dyeing properties.

SAFRANINE ($C_{21}H_{22}N_4HCl$)

was at one time a very important colouring matter for cotton dyeing and printing. It has lost much of its importance since the lowering in price of alizarin, and the introduction of other reds or scarlets in the dyeing of cotton.

It is produced on an extensive scale by the reaction of nitrous acid gas, or nitrites on suitable brands of aniline oil or salt; the production, which is an azo derivative, is then oxidised to the colouring matter, which is generally brought into commerce in the form of the HCl. salt, of the safranine base, either as a paste or in dry powder; therefore, this dyestuff is a basic product, and is applied in dyeing and printing in the same way as other anilines of the same class.

In cotton dyeing it is principally used for pinks, and especially for reds or scarlets in connection with either phosphine or chrysoidine.

Safranine is not fast against light, but stands moderately well against soaping. Scarlets obtained on cotton with safranine and phosphine on sumack and tin, or tannic and tartar emetic mordants, stand soaping pretty well, while scarlets produced by means of safranine and chrysoidine lose the latter, on soaping, leaving a blueish red behind.

Mixtures of safranine and chrysoidine are plentifully found in the market, and serve for production of reds on cotton yarn or cloth, imitating barwood reds very closely.

In calico printing safranine is sparingly employed for pinks; the shades produced stand soaping moderately well, but they do not stand light well.

PHOSPHINE

is a yellow orange dyestuff, which is very expensive, being produced in very small quantity as a bye-product in the manufacture of magenta or in the purification of rosanilin. It is consequently only sparingly used in dyeing and printing ; its employment being limited to mixing with safranine for the production of scarlets on cotton yarns.

INDULINES

are like the aniline blues, of two classes, either soluble or insoluble in water. They are produced from aniline which is converted into an azo product, and furnishes the colouring matter by treatment with aniline and hydrochloric acid in the same way as in the manufacture of aniline blues.

The commercial products are of different shades, from a very red-blue to a blue of indigo-like shade, the products soluble in water have very little interest for cotton dyeing, being principally used for wool. But the bluest variety, insoluble in water, but soluble in spirit, is to a certain extent used in calico printing in the form of a paste under the name of French grey ; and is fixed in printing in the same way as aniline blue. The shades produced stand light and soaping fairly well.

A spirit induline solution is sometimes used by dyers for producing imitations of indigo blues.

A special make of induline colour for printing has been recently introduced into commerce, and is applied in calico printing by means of tannic acid and ethyl tartarate, yielding shades which stand light remarkably well. This product was brought out by the Höchst printworks.

ROUBAIX BLUE is a derivative from induline, and gives a bluer shade both in dyeing and printing.

NEW BLUE D. of recent introduction (Cassella), is not largely employed in printing, but deserves attention at the hands of calico printers and dyers, as it yields shades similar to those obtained from indigo, which possess great fastness against light and soap.

NEUTRAL RED AND NEUTRAL VIOLETS

produce dull colours which have not found much employment either in dyeing or printing.

BISMARCK BROWN ($C_{12}H_{13}N_5 + 2HCl$)

is the first azo dyestuff which has been produced, and is known under the name of Manchester Brown. Nitro benzol is reduced by means of hydrochloric acid and iron filings into phenylen diamine HCl, and the latter yields the brown by treatment with nitrite of soda.

The azo product thus formed is thrown out from the solution by means of common salt, and filtered, dried, and brought into commerce in the form of a powder.

It is a basic dyestuff and readily soluble in water; it is employed principally for dyeing, and is only sparingly used in printing, as the shades produced are not fast.

It comes in commerce of different shades, often very largely adulterated with common salt.

CHRYSOIDINE

is produced also from phenylen diamine by a modification of the process employed in the manufacture of Bismarck brown; the dyestuff is soluble in water, of basic character, but has lost much of its former importance,

On cotton it yields orange colours, which are neither bright nor fast, and in printing it has no interest whatever.

FLAVANILINE.

is a basic yellow dyestuff recently introduced in commerce, and used to a moderate extent in cotton dyeing and printing.

VICTORIA BLUE (R & B)

are new dyestuffs which would be of great importance if they stood exposure to light, and are applied in the same way as other basic products.

AURAMINE $[C_6H_4N(CH_3)_2]_2CNH\ HCl$

is a very useful product both for cotton dyeing and printing, yielding shades pretty fast against soaping and light.

As it is the HCl salt of the auramine base, it can be fixed in the same way as the other basic products. In the dissolving of this dyestuff hot water can be used, but the solution must not be boiled, as the product decomposes. It can be used by the dyer and printer, not only as a self colour for bright yellows, but also for a great variety of compound shades; and in connection with safranine it gives scarlets preferable to those produced by means of chrysoidine.

RED CORALLINE

is a product of the reaction of ammonia on aurine, and therefore a phenol derivative. It is still employed to a small extent in calico printing, but it gives colours of very little solidity towards light and soap.

THE EOSINES.

These series of colouring matters may be considered as the most beautiful among the coal tar colours, but unfortunately they are exceedingly loose towards soap and light. They are generally employed for the production of fine pink shades in cotton dyeing, some of these imitating very closely those produced by means of safflower.

In calico printing they are sparingly used, and only for the production of those goods for the colours of which solidity is required.

The principal dyestuffs belonging to the eosine class are the following:

Eosine yellow shade.
Eosine blue ,,
Rose Bengal.
Phloxin.
Cyanosin.

they are all derivatives of *Fluorescëine,* a yellow dyestuff of itself of little value as a dyeing material, but possessing in a splendid degree the interesting property of fluorescence, that is, showing a diffeıent shade if viewed by transmitted or reflected light.

The yellow shade eosine, which is a bromine derivative of fluoresceine, shows the fluorescence to a high degree; this property is, however not so much shared by the blue shade eosine, which is an iodine derivative.

Of these eosines rose bengal gives the bluest shade, while the spirit eosines, or those only soluble in alcohol, give brighter colours than the water soluble, but are of less interest in cotton dyeing, and not used at all in printing.

THE AZO COLOURS.

This is the richest class of colours derived from coal tar, and a great variety of shades have been produced. Few of these products, however, have been found of practical utility for cotton dyeing or calico printing.

The azo colours may be divided into two classes, the basic and the acid colours; the basic products are either soluble, as for instance Bismarck brown and chrysoidine, which have already been mentioned, or insoluble in water but soluble in spirit.

The acid products are the sulphonic acid derivatives, and are of very great variety, beginning with yellow and following up the complete range of shades, viz:—orange, red orange, scarlet, red, blueish red, &c.

The insoluble basic azo colours have no importance either in dyeing or printing, but one or two of them are of interest, as they have been produced on the fibre by dyeing, and fast colours have been obtained by the methods patented by Holliday, Dawson and others.

The cotton is impregnated with a solution of naphtol in caustic soda, wrung, and then passed into a fresh bath containing the azo compound of any of the amines, such as aniline, toluidin, xylidin, naphthylamine, &c. The first of these, the aniline, gives a yellow, the second a yellow orange, the third a red orange, the fourth a scarlet of a yellowish hue, and the last a red; in other words different shades can be thus produced, varying from yellow to red.

Of these shades, however, only the reds have been found to be of any practical utility, principally those obtained by passing the cotton first through a bath containing a solution of naphthol in caustic soda, wringing, and passing into a new bath containing a mixture of the azo product obtained by a mixture of xylidine and naphthylamine in weak hydrochloric acid.

If the cotton has been mordanted with oleine or sulphonated oil, much brighter shades are produced. In fact by this method colours are obtained, both on cotton yarn and cloth, imitating closely those produced with alizarin.

These shades stand soaping, and especially chlorine, remarkably well, and the reds have been found especially useful for cotton yarns; the only drawback attached to this process is, that the colours are apt to rub, and the dyeing operations, although less expensive, are more difficult to conduct than the ordinary alizarin methods.

Grässler has attempted to produce steam azo reds in printing, but the method is little used.

Azarine is a bisulphite of sodium derivative of one of the insoluble azo reds, and has been introduced in dyeing and calico printing for the production of pink shades of great beauty. Reds can also be obtained from this product either by dyeing, or by applying it in printing as a steam colour. The shades produced are, however, not quite fast against soap, especially when exposed to light.

An interesting fact connected with this dyestuff is that it gives brown colours on iron mordants, for which it may find useful employment in the dyeing of cotton pieces printed with iron and alumina mordants, as in the madder styles. Azarine, however, as yet, is not largely employed.

THE SOLUBLE AZO COLOURS.

A great variety of these products are in the market under different names, which causes some confusion.

The products, however, employed in cotton dyeing or calico printing are only few, as the shades produced, although very bright, are very loose in washing or soaping, and are only employed for those goods which have not to be washed, consequently its use is limited.

The colours mostly employed are orange, yellow and red shades and the scarlets.

The following are some of the names under which these products are sold in commerce; they are obtained by different processes, but they all behave in the same way in dyeing and printing, and show the same looseness towards washing; the difference in their manufacture is of small interest to the consumer, while the difference of the processes, some of which are patented, are of great importance to the manufacturer, as they are produced in very large quantities and at very low prices, and are very largely used in wool dyeing, for which they have been found much more valuable than for application on cotton.

Tropeolines (oranges of different shades).
Oranges, No. 1, 2, 3, and 4.

No 2 being mostly used.

Scarlets, O., OO., &c.
,, G., R., RR., RRR., &c.
Crocein scarlets.
Fast red, B. & Y. shades.
Brilliant scarlet,
Biebrich scarlets.
Imperial scarlets, &c,

All these azo colours are found in commerce in the form of powders, readily soluble in water.

NEW CLASS OF AZO COLOURS.

The new class of dyestuffs are very interesting, because, unlike the others, they can be applied on cotton without the aid of mordants, and in a single bath.

The first of this class is

Congo Red, a derivative of benzidine, which is first converted into the azo compound and then reacted upon by the sodium salt of naphtylamin sulphonic acid.

The product is applied on cotton in a single bath containing soap, with or without the addition of phosphate or silicate of soda, the colour being fixed at the boil. The shade is a very fine one, but it does not stand light, although very fast against soaping. It has also the drawback of not standing acid, which turns it blue. This colour is so sensitive to acids that it has been utilized as an indicator for acids in such products as cannot be very well tested by other means; for instance, alum or sulphate of alumina, if containing any free acid will react at once on Congo red and convert it to blue.

BENZOPURPURIN RED is similar to Congo red, but faster to light, though it cannot be said to stand thorough exposure to it. It has also the property of being fast to soap, and is of a yellower shade than Congo red. A mixture of both will give very good results.

Benzopurpurin is a derivative of tolydine, and is first converted into azo product, and then treated with naphthylamin sulphonate of soda; in other words it is the homologue of the Congo red. It is not so easily affected by acids as the latter, and is in all respects a faster colour. This dyestuff, which is readily soluble, is applied on cotton in a boiling soap bath with phosphate of soda.

BENZOPURPURIN 4B is a product of a bluer shade, and seems to stand acids better than the ordinary product.

CHRYSAMINE is a yellow product, very soluble in water, and can be applied on cotton in the same way as other dyestuffs of the same class; viz., in a boiling soap bath and phosphate of soda.

The shades produced on cotton stand soaping and light fairly well.

AZO BLUE AND BENZO AZURINE constitute the last of this series of interesting new products, which, along with benzopurpurin and chrysamine, have been introduced into commerce by the Bäyer colour works.

They yield shades on cotton which are fast to soap and light as well as acids.

The shades obtained with these colours vary from light to dark blues, and if indigo blue shades are required, chrysamine is employed with benzo-azurine in the same bath. All these colours have been unsuccessfully tried in direct printing, but they have been found useful for dyeing cotton cloth in the different shades, the printing being done afterwards with aniline black stripes, or other patterns, thus forming a black pattern on red, yellow or light-blue ground.

INDO PHENOL.

Naphthol Blue is a derivative of naphthol and nitroso dimethyl aniline, and is of a certain interest for calico printing, in which it yields shades similar to those obtained by indigo, though not possessing the same fastness, but coming very nearly to it. The discovery of this product is due to Horace Koechlin, who was also the first to apply it in printing. It was afterwards studied by Witt, who called the attention of chemists to this interesting dyestuff.

Its behaviour towards acids is an impediment to the extended application of this dyestuff, since shades are destroyed even by weak acids.

In cotton dyeing it has not the slightest interest, as yet; in printing it is used only to a moderate extent. It is found in commerce generally in the form of a paste, which has been reduced by means of tin crystals and acetic acid, under the name of *Indophenol white paste.*

ARTIFICIAL INDIGO.

A method of producing indigotin artificially was discovered by Prof. Baeyer in 1880, and gave rise to much excitement, but the hopes and fears that the new artificial dyestuff would drive away the time-honoured indigo have not been yet realized, and there is, as far as can be at present judged, no probability of the most important of natural dyestuffs being driven out of dyehouses and printworks.

The artificial indigo has not been introduced into commerce as artificial indigotin, but as a product capable of producing it on the fibre.

The commercial product, which owing to its high price has never been largely employed, as it cannot compete with natural indigo, is the ortho-nitrophenyl-propiolic acid, $C_9H_5(NO_2)O_2$, which by reduction is converted into indigotin.

$$2C_9H_5(NO_2)O_2 + 2H_2 = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O$$

the reaction being effected on the fibre or cloth prepared with reducing agents, such as glucose or xantate of soda. It has so far more a theoretical than practical interest.

ALIZARIN.

Alizarin is, along with indigo, the most important dyestuff employed in cotton dyeing and printing, and on account of its low price its application becomes more and more extended every year.

The commercial product generally known as alizarin is very often a mixture of the latter with the other allied dyestuffs, flavopurpurin and anthrapurpurin.

The form under which commercial alizarin is sold is generally that of a paste, containing 20 per cent. of dry colouring matter; for the purpose of saving freight even 40 per cent. is prepared, and even preparations of dry alizarin have been recommended.

The manufacture of alizarin is conducted on a very large scale, the process generally followed relying first on the oxidation of *Anthracene* into *Anthraquinone*, which is then converted into a *sulphonic acid* compound, which, by fusion with caustic soda, is in its turn converted into alizarin.

ANTHRACENE ($C_{14}H_{10}$) is a solid hydrocarbon which is produced in very large quantities during the process of distillation of coal tar, and forms the raw material for the manufacture of alizarin and alizarin derivatives. After undergoing a purification it is converted into

ANTHRAQUINONE ($C_{14}H_8O_2$), by treating the purified and sublimed anthracene in fine powder, suspended in water, with bichromate of potash, or soda, and sulphuric acid, the reaction taking place as follows:

$$C_{14}H_{10} + O = C_{14}H_8O_2 + H_2O.$$

Anthracene. Anthraquinone.

After the oxidation has taken place the product is filtered and well washed, and after drying and undergoing a purification, first with sulphuric acid, and afterwards with soda, the product can be repurified by sublimation, and employed in the manufacture of purer products, while for cheaper alizarins it is not sublimed. Anthraquinone forms three sulphuric acid compounds, viz., *Monosulphonic Acid* and *Alpha* and *Beta Bisulphonic Acids;* and according as one or the other is produced a different result is obtained, since the monosulphonic acid compound yields pure alizarin, while the alpha bisulphonic acid produces flavopurpurin, and the beta yields anthrapurpurin.

Monosulphonic Acid of anthraquinone is produced if the temperature is raised to 160°, while the beta salt of the bisulphonic acid is formed by heating at 160° C., as for the monosulphonic product, but with an excess of fuming sulphuric acid; the alpha derivative is obtained by using a temperature of 185° C.

An interesting fact connected with this treatment is that it has stimulated the manufacture of sulphuric anhydride (SO_3), which is now a product of commerce.

The sulphonic acid compounds are ultimately obtained as sodium salts, and then converted into the respective colouring matters by fusion with caustic soda.

In the manufacture of alizarin the reaction which goes on in the fusing process is complicated by the production of hydrogen which takes place, which would react on the alizarin already formed, and reduce the same; it is therefore necessary to add a certain amount of chlorate of potash in the melting operation, in order to make up for the reduction effected by the hydrogen. The reaction which takes place is

$$C_{14}H_7O_2SO_3Na + 3NaOH = Na_2SO_3 + H_2O + C_{14}H_6O_2(ONa)_2 + H_2$$

Anthraquinon, Sulphonate of Soda. Alizarate of Soda

The industrial operation is conducted as follows: In a strong iron boiler, supplied with mechanical agitators, and capable of standing heavy pressure, are placed three to four parts solid caustic soda with sufficient water to dissolve the same, and then the necessary amount of chlorate of potash is added, with one part of the sodium sulphonate. After stirring the whole the vessel is closed and the temperature brought to about 190-200° C., and kept at that heat for 24 hours, when the formation of alizarate of soda takes place, and when the melt is taken out it is dissolved in water, and the alizarin precipitated by means of sulphuric or even sulphurous acid, then filtered, washed and pressed in a filter press, and made up with water to the desired strength.

ALIZARIN $C_{14}H_6O_2(OH)_2$, Bioxyanthraquinone. This is a bibasic acid, and forms salts which are either soluble or insoluble, according to the base with which it is combined; with alkalies it gives soluble alizarates, but with metallic oxides the salts are insoluble, and are utilized in the preparation of alizarin colours.

Commercial alizarin of blue shade is principally formed of pure alizarin and a small amount of the other two, flavo or anthrapurpurin. It is the pure alizarin which gives the bluest reds, while the yellower shades are obtained by the other two products alone or mixed with alizarin.

The principal combinations of alizarin with metallic oxides are the following:

Red with alumina.
Purple or violet with iron.
Violet with calcuim or barium.
Violet with lead.
Red orange with tin, &c.

The most important of these precipitates or lakes are those of alumina, and next those of iron. The alizarates have been closely investigated of late by Liechti and Suida, who have published some very interesting results on the alizarate of alumina and those of alumina and calcium, of which the most important result is that, according to the combination found, the lake is more or less soluble in water, for instance, the neutral alizarate of alumina is soluble in water, while basic alizarates are either little soluble or insoluble, according to their degree of basicity.

The iron lakes of pure alizarin are of a more violet and brighter tone than those produced by anthra or flavopurpurin, which are of a brownish hue. The chromium alizarates are also interesting, and find useful employment in the fixation of alizarin by steaming, An important fact connected with the alizarates is that most of them are soluble in caustic soda lye, and therefore give the means of producing a printing colour which can be fixed on the cotton by steaming, for instance, a red can be produced by dissolving the alumina alizarate lake in ammonia or caustic soda, and adding a little olive oil and acetate of lime; the whole properly thickened is printed, and the cloth then steamed, when a fair red is produced.

The alizarin lakes are generally produced by precipitating a solution of alizarate of soda by means of alum or sulphate of alumina, and a brighter colour is obtained if the precipitate, after filtration, is boiled with a small amount of acetate of calcium or alizarin oil.

ANTHRAPURPURIN $C_{14}H_5O_2(OH)_3$ Trioxyanthraquinone. Is also called Isopurpurin, and is the product of fusion of the beta of the disulphonate of soda with caustic soda.

FLAVOPURPURIN possesses the same formula, and is also a derivative of the bisulphonic acid salt, but of the alpha variety.

Both flavo and anthrapurpurin are contained in the commercial alizarins of yellow shade, more or less mixed with pure alizarin. As a rule, the reds obtained with the alizarin yellow shade are yellower than those produced by means of pure alizarin, and, as stated before, the violets are of a browner shade.

The yellower shades produced on cotton by dyeing or printing, are not as fast as the blue or medium shades.

Commercial alizarin is distinguished according to its shades, as B., 2B., 3B., for blue; and Y., 2Y., &c., for yellow shades.

The application of alizarin is a very important one, equally so for dyed as for printed colours, and it forms a very important speciality in the dyed and printed Turkey-red goods.

In testing commercial samples, the amount of water it contains must first of all be estimated, or the amount of dry colouring matter it yields when dried. The ash also must be estimated, and should not be more than 1%. The colouring power must also be tested either by dyeing or printing. One point of importance connected with the use of alizarin is that by long standing in the casks it settles at the bottom, forming there a thick paste, while at the top of the cask it is very watery; if, therefore, the contents of the cask are not well shaken up, the alizarin first taken out will be much weaker than that which remains. Alizarin must also be free from little lumps; in fact, between the fingers it must show an impalpable soft pigment, and quite free from grit if used as a steam printing colour.

ALIZARIN ORANGE. [$C_{14}H_5NO_2O_2(OH)_2$]

Nitroalizarin is produced by converting alizarin into a nitro compound, and is brought in commerce also in the form of a paste containing 10 or 20% dry colour. It has not proved as useful in printing and dyeing as might have been expected, but it deserves more attention at the hands of printers. The oranges it produces on cotton are fast, but not very bright, and are produced by the steam printing method, using alumina mordants; the sulphocyanide being most appropriate. For compound shades it ought to be very useful.

ALIZARIN BLUE ($C_{17}H_9NO_4$)

would no doubt be found very useful in printing if it could be obtained at a lower price. It is a derivative of nitroalizarin, from which it is obtained by treatment with glycerine and sulphuric acid. The commercial article originally introduced was in the form of a 10% paste, but the product now sold is the bisulphite of soda derivative, and is soluble in water. It is sold in the form of a brown powder, under the name of alizarin blue S.

It is most interesting as a steam colour, fixed with acetate of chromium, but for dyeing it has not the same importance, since it cannot compete with indigo in fastness, nor with other coal tar blues in price.

The only method of testing it is by a practical trial by printing. Although alizarin blue may be considered a fast colour, it is not absolutely fast against light, but stands soaping remarkably well, and is not so easily affected by oxidising agents as indigo.

GALLEIN AND CERULEIN.

Although sometimes classed among the alizarin colours, these really belong to the eosines, but they behave in point of fastness and method of fixation like alizarin.

Gallein ($C_{20}H_{10}O_7$) is the product of the reaction of phtalic acid anhydride with pyrogallic acid, at about 200° C.

It is a violet dyestuff, which is, however, only sparingly employed by itself for producing violets or brown greys, but serves as the raw material for the production of

Cerulein ($C_{20}H_8O_6$).—This is obtained by heating with a large excess of sulphuric acid at about 200° C., and when the reaction is complete the product is poured into water, filtered and washed. The reaction which takes place in the treatment with sulphuric acid is the elimination of one molecule of water.

$$C_{20}H_{10}O_7 - H_2O = C_{20}H_8O_6$$

The dyestuff was originally brought into commerce as a 10% paste; but lately the bisulphite compound has been produced, and is sold as a powder soluble in water, under the name cerulein S.

Either the one or the other yield a fast olive green, which is greatly utilized in calico printing with excellent results, being connected with alizarin and other fast steam colours.

Only a practical trial can be employed as a test for this dyestuff.

Gallocyanin is a dyestuff, so far, very sparingly used in calico printing, for producing fast violet shades.

NEW COLOURING MATTERS.

Several new products have been recently introduced in commerce which produce fast shades by printing. Of these blue forms the principal colour, and as many as four new blue dyestuffs or preparations, derivative of coal tar, have been introduced. They are the following:

Blue D. (Cassella's)

Induline Blue Preparation of the Höchst colour works.

Indigen (Fr. Baeyer, Elberfeld colour works).

A Blue Preparation for producing a fast blue, imitating indigo, on Turkey-red dyed goods.

All these products are fixed by the intermediate of tannic acid, of which, recipes will be given in the practical part.

Of other new colours, two products—

Galloflavine and Anthracene Brown (of the Badische, aniline, and soda fabric) are very interesting, as they yield fast shades in printing, for which they can be applied in the same way as alizarin, the shades produced possessing the same degree of solidity against light and soap. Galloflavine yields good lemon yellows on alumina or chrome mordants, and nice olives with iron.

No doubt this dyestuff will be found very useful in printing in fast styles in which chrome-yellow is almost the only one which can at present be applied, and the chrome yellow has some drawbacks which would cause a substitute to be much welcomed by printers. Galloflavine would be probably found a suitable one, only the shade is not quite as bright as chrome yellow.

Anthracene Brown yields with alumina mordants a reddish brown, and with chromium mordants a tobacco brown, both of great fastness.

Nitroso Resorcine (Durand and Huguenin) is also a new product, and yields dull greens of great fastness, which are found useful in printing, and in the dyeing of cotton, for which it is used in the production of fast blacks.

MORDANTS.

ALUMINA MORDANTS.

Sulphate of Alumina ($Al_2(SO_4)_3 + 18H_2O$) is very extensively used both in dyeing and printing, and comes now in commerce in large quantities and in different degrees of purity.

By some firms it is manufactered of very good quality and almost completely free from iron, so that it can be in many cases employed instead of alum for alizarin-red dyeing or printing. It is obtained as a bye-product in the manufacture of soda from cryolite, but principally from bauxite, and in many cases from ordinary clays by treatment with sulphuric acid.

The product comes in commerce generally in the form of blocks or fused masses. It contains 15 per cent of alumina, and is a more advantageous product to use than alum, as it is cheaper in price and contains more Al_2O_3; if not free from iron it cannot be used for the dyeing and printing of those colours in which the slightest amount of iron is injurious. Good qualities of sulphate of alumina are generally subjected to a process of purification to eliminate the iron.

Sulphate of alumina has the property of forming basic salts when treated with alkalis in solution. These basic sulphates of alumina thus formed are capable of acting as mordants, and depositing alumina on the fibre.

The mordanting property of the basic sulphates of alumina has been long known, but it is due to Messrs. Liechti and Suida that we have more definite and exact knowledge of the compounds formed, and of their property, especially in respect to their degree of dissociation. In preparing these basic solutions of basic sulphate of alumina, as a rule, either carbonate or bicarbonate of soda is used. Care must be taken not to add either of them all at once, but in small portions at a time, as carbonic acid is evolved by the reaction, and by frothing over some of the solution may be lost, since sulphate of alumina reacts as an acid, and drives away the carbonic acid. The more basic the solution of sulphate of alumina the more readily it will dissociate; for instance, very basic solutions will precipitate out of the solution at about 70° C., even when diluting the original strong liquor with water, while less basic salts require a lengthy boiling before they begin to dissociate.

The reason why the commercial sulphates of alumina have not found more extensive employment is that they vary considerably in the amount of Al_2O_3 they contain. Some brands also contain free acid, and this is decidedly an objection in many cases.

The active product in the sulphate of alumina is the alumina Al_2O_3, or rather the hydrate of alumina $Al_2(OH)_6$, which is capable of forming combinations with colouring matters, and therefore in estimating commercial samples the amount of Al_2O_3 must be determined by the ordinary methods of quantitative analysis. As the presence of iron is very objectionable, if the sulphate of alumina is utilized in red dyeing with alizarin, it must be tested for this impurity by dissolving a small amount in water, in a test tube, and testing with solutions of ferro or ferricyanide of potassium, when a blue precipitate will at once show the presence of iron.

It can also be detected by adding to the sulphate of alumina solution a small amount of tannic acid solution, or even logwood liquor, when the presence of iron will be at once apparent by the black or deep grey colouration or precipitate.

The free acid can be easily detected by means of a solution of Congo red, which is turned blue by free acid, and by means of this reaction it can even be estimated.

A good quality of sulphate of alumina will contain about 15 per cent. Al_2O_3.

ALUM.

Alum has been employed in tinctorial arts from a remote period. It is very extensively used now; and up to a few years ago was preferred to the cheaper sulphate of alumina, because the quality of the latter was not so good as it is now manufactured, and always contained such an amount of iron as to make it unfit for the production of reds. For Turkey-red dyeing, however, alum of a very pure quality, known as Turkey-red alum, is still employed in preference to the sulphate of alumina.

Although ammonia alum is also found in commerce, the potash salt is the one extensively used, and can be met in the form of fine crystals of very great purity; it is also sometimes sold in powder form.

POTASH ALUM ($Al_2 (SO_4) {}_3K_2SO_4 + 24H_2O$) contains 10·83 per cent Al_2O_3; it is, as will appear from the formula, a double salt of sulphate of alumina and potash, the latter being, in a certain sense, a useless product, as it does not enter chemically in the mordanting of the cotton. But in the case of basic sulphate of alumina solutions, the presence of sulphate of potash, as well as that of sulphate of soda, helps indirectly in the mordanting operation by hastening the precipitation of the mordant on the fibre. Alum dissolves in 18 parts cold water and in less than one part boiling water.

The chemistry of the employment of alum and its derivatives in dyeing and printing has been very well studied, not only recently, but also by the past generation of chemists; but the employment of this important series of mordants is better based on long practical experience than on exact theoretical principles, and this will be the case until the mysteries connected with some of the dyeing processes for cotton have been cleared up.

From alum basic sulphates of alumina have been very largely used in cotton yarn and piece dyeing, principally

Turkey-red dyeing; they react in the same way as those obtained from the sulphate, but are affected by the presence of the sulphate of potassium to a certain extent.

Alum may be tested for iron by solutions of ferro or ferri-cyanide of potassium, or by meams of tannin or logwood solutions. Although well crystalised alum can always be relied upon, the estimation of Al_2O_3 may be found of advantage.

ACETATES OF ALUMINA.

These are generally obtained by double decomposition (*a*)—of alum or sulphate of alumina with acetate of lime:

$$Al_2(SO_4)_3 + 3Ca(C_2H_3O_2)_2 = 3CaSO_4 + Al_2(C_2H_3O_2)_6$$

(*b*)—of alum or sulphate of alumina with acetate of lead:

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = PbSO \ + Al_2(C_2H\ O_2)_6$$

(*c*)—by precipitation of hydrated alumina by means of sodium carbonate, or caustic soda and dissolving in acetic acid:

$$Al_2(SO_4)_3 + 6NaOH = 3Na_2SO_4 + Al_2(OH)_6$$
$$Al_2(OH)_6 + 6C_2H_4O_2 = Al_2(C_2H_3O_2)_6 + 6H_2O.$$

In proportion to the quantity of sulphuric acid removed, different products are obtained, varying in their chemical composition, and also in the way they behave in the fixation of the alumina mordant on the fibre. A complete range of products can thus be obtained in solution, beginning with the normal acetate, and following with the sulphate acetates of different composition and behaviour, according to the amount of combined sulphuric acid still left in them.

The chemistry of the acetates of alumina has been thoroughly investigated by Professors Liechti and Suida, who have thrown considerable light on the behavour of the different preparations, principally in regard to the way they dissociate and allow the alumina mordant to be fixed on the fibre.

Normal acetate, when applied on cotton and dried, yields 50 per cent. of available alumina, while a basic acetate of the formula $Al_2(C_2H_3O_2)_4(OH)_2$, containing also the sulphate of soda, gives up almost the whole amount in alumina when applied in the same way.

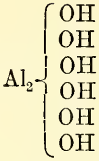
In the preparation and employment of the acetate of alumina mordants long practical experience is relied on rather than theoretical principles, but it will be well in all cases to bear in mind the most recent results obtained by chemists.

The following considerations on these mordants will be found useful:

The formula $Al_2(C_2H_3O_2)_6$, or rather neutral acetate, is of most use in steam colour printing, because it does not decompose so readily as the basic salts.

In the preparation of steam colours for printing, especially those in which alizarin enters, it is required to have a mordant which would only be decomposed by steaming, in order that the lake may be well fixed on the fibre, because if the mordant precipitates in the colour before it is printed, some of the lake is at once formed, and consequently it is not fixed in its entirety on the cloth, and poorer colours result. For this reason it is made very often a rule, when printing steam colours with acetate of alumina, to have a certain amount of free acetic acid, in order that no dissociation or precipitation of the mordant or lake takes place before the colour is printed. By this means the solution of the mordant penetrates the fibre, but is only precipitated on it by the subsequent operation of steaming.

The basic acetates of alumina can be employed in printing if they do not dissociate too readily, and they are of advantage when printed on cloth which is afterwards dyed; as for instance, in the case of alizarin dyeing in the so-called madder styles. But the utility of these basic acetates of alumina will be found principally in the dyeing of plain colours on cotton. In addition to the basic acetates there are also the basic sulphate acetates, the formation of these different compounds being easily made clear when looking at the formula of hydrate of alumina ($Al_2(OH)_6$),



$$Al_2\begin{cases}OH\\OH\\OH\\OH\\OH\\OH\end{cases}$$

when the group OH can be displaced by an acid group.

In the basic sulphate-acetates it is also observed that the more basic they are the more readily they dissociate by heating. It is also of importance to note, that when applied on cotton and dried, they leave on the fibre the whole of the alumina they contain. The basic sulpho acetate giving the best results has the formula :

$$Al_2(SO_4)\ (C_2H_3O_2)_3OH$$

There are many preparations of alumina mordants in commerce, some of them of good quality and answering well for special purposes, which are known under different names; such as acetate of alumina, red liquors, red mordants, &c. It is, however, well to prepare the alumina mordants as they are required, not so much as a point of economy, but in order to work with a known product, especially reliable in point of strength.

The acetates and sulpho acetates are tested for the amount of Al_2O_3 they contain; but in order to ascertain if a mordant is suitable for one purpose or another, it is always well to make a practical dyeing or printing trial on a small scale.

In practice the mordants are generally prepared to show a certain degree of the Tw. or Bé.

Sulphate of Lead is a bye-product in the manufacture of acetate and other acetates of alumina, and is utilised for different purposes, such as the preparation of resists for indigo blue dyeing; sometimes as a white pigment, and sometimes as a raw material for the manufacture of chrome yellows.

When large quantities are obtained, especially if produced in the manufacture of acetate, and, therefore, not of as good a colour as the one produces in the manufacture of acetate of alumina, it can be preferably used for the recovery of lead by heating a quantity of paste, corresponding to 160 parts dry sulphate of lead with 200 parts water and 18½ parts iron filings, until the white disappears completely. In this operation the reaction is the following:

$$PbSO_4 + Fe = FeSO_4 + Pb.$$

when besides metallic lead, which is formed as a heavy powder, the sulphate of iron remains in solution, and is completely removed by filtration and washing before the metal is fused.

NITRATE OF ALUMINA ($Al_2(NO_3)_6$) is not largely used, but is often employed in the preparation of colours for steam alizarin reds, which are obtained of a brighter and yellower shade, owing probably to the formation of a small amount of nitric or nitrous acid by the action of steaming. It is generally obtained by double decomposition, by means of nitrate of lead and sulphate of alumina, or alum.

SULPHOCYANIDE OF ALUMINA ($Al_2(CNS)_6$) is extensively used for steam alizarin reds, as brighter shades are produced than by means of the acetates.

This is probably due to two causes; one being that sulphocyanides prevent the injurious effect of iron, which may have been dissolved from the steel doctor of the printing machine by the colour; the other reason, probably, is that as the sulphocyanide of alumina only decomposes by steaming, no lake is precipitated in the colour before printing or steaming; in other words, it allows the amount of the alizarin and the alumina mordant to be mostly fixed on the fibre.

It is generally obtained by double decomposition of sulphocyanide of calcium, or better, barium, with sulphate of alumina, according to the following equation:

$$Al_2(SO_4)_3 18H_2O + 3Ba(CNS)_2 2H_2O = Al_2(CNS) + 3BaSO_4 + 24H_2O.$$

ALUMINIUM CHLORIDE (Al_2Cl_6) is never employed in calico printing, but recently an *Aluminium Chloride Acetate* has been recommended by Liechti and Suida for the preparation of steam alizarin-reds, when very good results are obtained, probably because this salt is only decomposed when steaming.

It can be prepared by treating sulphate of alumina with acetate of lead and barium chloride.

Aluminate of Soda, although known a long time under the name of alkaline mordant, has up to a few years ago been very little used. It is more largely employed in the dyeing of plain alizarin-reds, and as a printed mordant for producing dyed alizarin-reds and pinks. It will, no doubt, eventually be found useful for several purposes in calico printing.

It is associated with the glucose direct indigo printing process for producing patterns of red and blue, and is generally prepared by dissolving precipitated hydrated alumina, or commercial dry alumina, in caustic soda ; or it can be obtained by dissolving alum, or sulphate of alumina in boiling water, and adding enough caustic soda until the precipitated alumina is redissolved, when it is allowed to cool in order that the sulphate of sodium may crystalise out, and the filtered solution is then ready for use.

This alkaline alumina mordant is generally thickened with dextrine, but can also be mixed with starch paste ; it does not require steaming or ageing for the fixation of the alumina it contains, as this is effected by passing the material, padded or printed with this mordant, through a bath containing a solution of sal-ammoniac, or chloride of ammonia, or other salts ; for instance, alum or sulphate of alumina, and even zinc salts.

Pieces printed or mordanted with aluminate of soda, when long exposed to the atmosphere, attract carbonic acid, and the aluminium is fixed to a large extent on the fibre.

It is not unlikely that the passage of pieces, printed with aluminate of soda and other similar alkaline mordants, through a box containing carbonic acid gas, would fix all the alumina they contain.

There is no doubt that both the aluminate of soda and other alkaline mordants will be largely used in future in printworks, since they would allow the old madder or alizarin dyed styles to be produced in a different way.

HYDRATE OF ALUMINA ($Al_2(OH)_6$).—This product, which has existed for some years in commerce as a gelatinous paste, is now sold in a dry state and of very great purity.

It can be employed either for the preparation of acetates by dissolving in acetic acid, or used for the preparation of aluminate of soda.

If used for red the product must be free from iron, for which impurity it should be tested.

IRON MORDANTS.

(FERROUS AND FERRIC SALTS.)

SULPHATE OF IRON, COPPERAS, GREEN VITRIOL. — Ferrous sulphate ($FeSO_4 + 7H_2O$) is produced on a very large scale by the utilisation of waste sulphuric acid and iron scraps, or as a bye product in different manufactures, and is found in commerce generally in the form of greenish crystals, dissolving in 1½ parts of water. When long exposed to air it undergoes oxidation, some of the ferrous salt being converted into ferric salt. Copperas is one of the cheapest of chemical products, but is sometimes adulterated with Glauber salt. It is well to estimate the amount of iron it contains in the form of ferrous salt by means of the permanganate of potash solution. The sulphate of iron serves as a raw material for the manufacture of iron mordants, principally the acetates, nitrosulphates, &c., and is employed as such pretty largely in the dyeing of cotton.

ACETATE OF IRON ($Fe(C_2H_3O_2)_2$,) (*Ferrous Acetate*), is very extensively used in cotton dyeing, but more especially in calico printing, where along with acetates of alumina it is found of great utility in the fixation of several colouring matters on the fibre, either by dyeing or direct printing.

It is obtained by different processes, either by double decomposition from lead or calcium acetates with copperas, or by dissolving iron filings in acetic acid, or rather in the pyrolignous or wood acid of commerce, which is an impure quality of the same acid, as for instance

$$FeSO_4 + Ca(C_2H_3O_2)_2 = CaSO_4 + Fe(C_2H_3O_2)_2,$$

or

$$Fe + 2C_2H_4O_2 = Fe\,(C_2H_3O_2)_2 + H_2.$$

The commercial articles are known under different names, such as black iron liquor, pyrolignite of iron, &c., and are of different strength and quality, being in some cases not pure acetates, but having a certain amount of copperas in the solution.

For this reason it is necessary to first estimate the amount of iron contained in the samples, and determine at the same time the amount of sulphuric acid (if any) it contains.

The estimation of the amount of iron is better effected by gravimetric analysis, as if the volumetric method by the permanganate process is used the result is not satisfactory, since a certain amount of the permanganate solution would be reduced by the organic matters generally accompanying wood acids and acetates.

In estimating the iron in these acetate of iron samples, they are boiled with nitric acid in order to convert all the ferrous into the ferric salt, and the precipitation is then effected by means of ammonia, the Fe being estimated ultimately as Fe_2O_3.

It is also advisable to test the iron acetates by a practical trial, by dyeing or printing. These mordants are not only used for the fixation of colours, but also for the production of buff shades in printing.

FERRIC SULPHATE ($Fe_2(SO_4)_3$) is very seldom employed in cotton dyeing, and never in printing.

It is obtained by the oxidation of copperas when treated with a mixture of nitric and sulphuric acid, or by dissolving oxide of iron in weak sulphuric acid.

It can also be obtained in solution as a basic salt, and in this form can be employed for cotton dyeing, for producing buffs, or for blacks in combination with logwood and sumach.

IRON ALUM ($K_2Fe(SO_4)_4 + 24H_2O$) is scarcely ever employed in tinctorial arts.

FERRIC NITRO-SULPHATES are found in commerce under the name of nitrate of iron, and are obtained by means of copperas by treatment with nitric acid. The commercial products vary considerably in the amount of iron and nitric acid they contain.

It is principally used in dyeing, scarcely ever employed in printing.

NITRATE OF IRON (*Ferric Nitrate*), only used for dyeing, scarcely ever in calico printing. It is obtained by dissolving scrap iron in nitric acid, and is generally employed in the production of buff shades, or in dyeing of blacks on cotton.

IRON ALKALINE MORDANT, although not largely used at present, will no doubt be found capable of more extensive application in future, principally in printing.

It is generally obtained by treating a solution of an iron salt with caustic soda and any other product which will prevent the precipitation of the iron oxide, such as glycerine, glucose, tartaric acid, &c.

As a rule glycerine is employed for the purpose, by taking caustic soda or ammonia and nitrate of iron. It is as yet not explained which reaction takes place.

This iron mordant in solution can be employed both for mordanting cotton for plain dyeing or for the production of plain shades, and also for printing.

CHROMIUM MORDANTS.

There are two classes; those derived from chromic acid and those obtained from chromic oxide (Cr_2O_3) or sesquioxide.

Bichromate of Potash ($K_2Cr_2O_7$) is produced in very large quantities, and comes into commerce generally of good quality, in well crystallized form.

In the manufacture of this product chrome iron ore is employed as the raw material, which is oxidized in reverberatory furnaces in connection generally with carbonate of potash and lime, the chromate of calcium obtained being decomposed by means of sulphate of potassium, the neutral chromate of potassium being then converted into the bichromate by the addition of sulphuric acid, and the solution evaporated to the crystallisation point.

It is employed both in dyeing and printing for two special purposes, either for the production of insoluble chromates, principally chrome yellows and oranges, or as an oxidiser or fixer of certain colours, such as catechu, logwood blacks, blues, greens, &c.; and is also found useful for the further oxidation of aniline blacks, &c.

It is also largely employed in chemical industry for the production of pigments, or, by its high power of oxidation, the manufacture of artificial alizarin, &c.

Its employment in the dyeing of cotton with aniline black is too well known to require any special mention. As a powerful oxidizer it is found very useful in the discharging of indigo in printing, for which purpose it is extensively employed.

The commercial article, if of good quality, must be of well crystallised form, of a reddish orange colour; as chromic acid is the acting agent in the product, when testing the amount of the chromic acid must be estimated.

Bichromate of potash dissolves in 1½ part of water; is also often found in commerce in powder form, but in many cases adulterated.

Bichromate of Soda ($Na_2Cr_2O_7$) is now largely employed in place of the potassium salt, being cheaper; containing in the same weight a larger amount of chromic acid.

It can be used in the same way as the potassium salt with advantage, provided it can be obtained of good quality, but some brands of this new product have not been found to possess the purity of the ordinary bichromate of potash.

Although it has the advantage of cheapness it has the drawback that it is very deliquescent, readily attracting moisture from the atmosphere, and when exposed for a long time in damp places it has been found to attract so much water as to form a solution and run out of the vessel if any leakage was present, consequently in using this salt it should be kept in closed vessls, and not exposed to dampness.

It has one advantage over the potassium salt, and that is its greater solubility in water. When obtained of good quality it will be found a very good and advantageous substitute for bichromate of potash.

In the manufacture of bichromate of soda the neutral chromate of soda (Na_2CrO_4) is first obtained by heating in a reverberatory furnace six parts chrome iron ore with three parts soda ash and three parts chalk. The mass is thrown in water while still hot, and the lye thus produced is evaporated to 112° Tw. in iron vessels, and then poured in leaden vessels to crystallise. A product is obtained of the formula $Na_2CrO_4 + 10H_2O$, which if dried in a stove at about 30° C. loses all its water of crystallisation, and gives a canary yellow powder. The bichromate is obtained from this neutral chromate by dissolving in hot water, and then adding sufficient sulphuric acid to convert it into the bichromate, which is seen by means of iodide starch paste, which is turned brown at the end of the reaction; then enough neutral chromate is added to the solution so as to obtain a product containing 72 per cent. chromic acid. After cooling, when the sulphate of soda crystallises out, the liquor is removed and evaporated to dryness in iron boilers by constant agitation. The ultimate product, which is a mixture of the bichromate with the neutral salt, is less hygroscopic than the pure bichromate, which is thus obtained in the form of egg-sized lumps which, being ground, forms then the commercial article. It is interesting to note that the bichromate of potash is less poisonous than the sodium salt. The commercial bichromate of soda contains about 72 per cent. chromic acid.

For testing in addition to the estimation of the chromic acid, it is necessary in all cases to make a practical trial in dyeing or printing.

CHROME ALUM ($K_2Cr_2(SO_4)_4 + 24H_2O$) is produced in a very large quantity as a bye product in the manufacture of alizarin and other industries, and forms the raw material for the manufacture of the majority of the chromium oxide mordants. The commercial product is estimated for the amount of Cr_2O_3 it contains by gravimetric analysis, and the amount of water is also taken into account. It should not contain any product insoluble in hot water.

ACETATE OF CHROME ($Cr_2(C_2H_3O_2)_6$) is one of the most important of the chromium preparations, and can be obtained :—

By the same processes by which acetate of alumina is produced, viz.:—By double decomposition with lead or calcium acetate, and chrome alum, or sulphate of chromium.

By treating a solution of chrome alum with carbonate of soda and dissolving the filtered and pressed precipitate in acetic acid.

From bichromate of soda or potash by reduction with sugar and acetic acid.

On account of the great stability of this compound it is never employed in cotton dyeing, because it does not yield the oxide to the fibre as the corresponding aluminum mordant does, but is very largely employed in printing, where it has found very extended employment in the last few years.

As a rule it is prepared in printworks, but is also found in commerce in large quantity.

The chromium mordants have also been thoroughly investigated by Liechti and Suida, from whose research it is shown that the normal chromium acetate is of such stability that it can be boiled and even evaporated to dryness without undergoing much change, as even if dried and heated to 230° C. it is still capable of going in solution. This fact readily explains why acetate of chrome applied alone on cotton does not fix any appreciable amount of mordant on the fibre.

The basic acetates of chromium are not largely employed in cotton dyeing, but they might be found useful to a certain extent as the basic salt:

$$Cr_2(C_2H_3O_2)_3(OH)_3$$

which is obtained by the addition of a corresponding amount of sodium carbonate to the normal salt, and when applied on cotton yields 66 per cent of the Cr_2O_3 originally contained in the solution.

The commercial acetate of chrome shows something about 30° Tw., but it is always well to make an estimation of Cr_2O_3 by gravimetric method.

NITRATE OF CHROMIUM ($Cr_2(NO_3)_6$) is very often used in calico printing, and can be prepared by double decomposition of the nitrate of lead and chrome alum; sometimes it is produced by dissolving the precipitate obtained from chrome alum solution and carbonate of soda by nitric acid; in this case, however, it must be observed that no free nitric acid must be left in the solution. This is easily accomplished by using such a quantity of nitric acid as will not dissolve all the hydrate of chromium.

NITRO ACETATE OF CHROMIUM is extensively used in printing, and is obtained by mixing the acetate with the nitrate solution, or by double decomposition of the chrome alum with the necessary amount of acetate and nitrate of lead. It is very often produced from bichromate of potash or soda, by reduction with glycerine, while nitrate and acetic acids are also employed for the production of the nitro acetate salt.

Sulphocyanide of Chromium has been recommended of late for steam colours; it is produced in a similar way to the corresponding alumina salt, and behaves in a similar manner.

CHROMIUM ALKALINE MORDANTS.

These mordants have attracted considerable attention in recent times, and have been recommended for the preparation of cotton to be dyed afterwards with those colouring matters which give insoluble combinations with oxide of chromium, but they have not been largely used, principally on account of their high price.

In the practical recipes will be found the method for the preparation of an alkaline mordant by means of glycerine and caustic soda lye.

A cheaper method has been recommended by H. Schmid, and has been successfully tried by the author. It consists in dissolving the precipitated hydrate of oxide of chromium in caustic lye.

The proportions being as follows:—

Oxide of chromium paste	17½ lbs.
Caustic soda lye (45° Tw.)	4 gallons.
Water	1 to 1½ ,,

150 parts of this composition correspond to 100 parts of chrome alum, for which 32 parts of ammonia soda have been employed for the precipitation of the hydrate of chrome. The alkaline mordant so prepared contains 10 per cent. Cr_2O_3.

This mordant is, however, not very stable, and easily undergoes decomposition, but by the addition of more caustic soda it can be kept longer. Cotton is mordanted in this bath, and then either left to lay 12 hours or fixed at once by a passage through the steam ager for one or two minutes, and after a good wash is ready for dyeing.

Another method of fixation consists in passing the mordanted cloth through a bath containing a metallic salt, such as copperas or sulphate of copper, or even alum or chrome alum, when another metallic oxide is thrown down on the fibre, and in this way different shades can be produced.

On account of the large amount of caustic soda contained in this alkaline mordant, the cotton is to a certain extent Mercerised.

TIN MORDANTS.

These mordants are employed as stannous or stannic salts, the latter mostly for cotton dyeing.

Stannous Chloride—Tin Crystals ($SnCl_2 + 2H_2O$), is also known as tin salt, &c. The commercial article varies considerably in the quantity of tin it contains, being very often adulterated with other chlorides. A pure product contains from 50 to 52 per cent. of metallic tin.

The production of tin crystals is important, as the product is pretty largely used both for wool and cotton dyeing. It is obtained by dissolving metallic tin, previously feathered, in hydrochloric acid, the solution being afterwards concentrated to the crystallising point.

In commerce, stannous chloride is also very often sold in solution in water according to its degree of Tw., which, however, is no sure indication of its strength, since common salt or other chlorides, which are sometimes added, would raise the degree of Tw., and consequently, either in the case of tin crystals or the commercial solutions, which are known under different names, it is as well to estimate the amount of metallic tin by volumetric analysis. Of the commercial solutions the muriate of tin shows about 60° Tw., while the double muriate is sold at 120° Tw.

Stannous chloride, either by long standing or exposure to air, or even by strong dilution, is apt to form a basic product, and this is the reason why sometimes commercial tin crystals, when dissolved in water, show a milky appearance, due to the presence of a certain amount of the basic chloride or oxychloride, instead of forming a thoroughly clear solution. But a clear solution can immediately be obtained by adding a small amount of hydrochloric acid and a little tin.

In calico printing tin crystals are pretty extensively used in the preparation of printing mordants in colours for dyed or steam alizarin reds, &c., because the presence of tin imparts more brightness to the reds, and gives a yellower hue than if alumina alone is used.

OXALATE OF TIN ($Sn(C_2O_4)_2$) is generally produced in the works where it is used by precipitating the hydrate out of a solution of tin chloride by means of carbonate of lime, and afterwards dissolving the precipitate in oxalic acid.

The proportions are about as follows :—

200 grs. stannous chloride, 15° Tw.................... 20lbs.

are dissolved in water, and then

15 parts of finely ground chalk.......................... 1½lbs.

is added in small quantities at a time. After stirring well the precipitate is allowed to settle, and washed with water by decantation until the water does not show the presence of lime when tested with sulphuric acid.

Then the precipitate is dissolved in a solution of

10 grs. crystallised oxalic acid .... 1lb.

in

100 grs. water .... 1 gal.

the whole being heated to about 50°C., the whole volume of the mordant is made up to

200cc... 2 gals.

Oxalate of tin is employed in connection with alumina mordants in the preparation of steam alizarin reds, for which, also, the

CITRATE OF TIN, which is prepared in a similar way by employing citric instead of oxalic acid can be used.

SULPHOCYANIDE OF TIN ($Sn(CNS)_2$) has also been employed in the preparation of steam alizarin colours along with alumina, and it gives yellower shades of a very pure and fiery tone. It is prepared from the oxalate of tin mordant, described above, by treating the

200cc. oxalate of tin solution .... 2 gals.

with a solution of

15 grs. sulphocyanide of calcium .... 1½lbs.

in

50 grs. water.. ½ gal.

Acetate of Tin ($Sn(C_2H_3O_2)_2$) is sometimes used in printing in preparing steam alizarin colours with alumina, but on account of the lead it generally contains, owing to its method of preparation, it is seldom employed. Its preparation consists in decomposing a solution of tin chloride by means of acetate of lead; when the acetate of tin is found in the solution and the chloride of lead is thrown down, the latter, however, is not wholly insoluble, and hence the mordant contains always a small amount of lead. The acetate of tin is very readily decomposed, and must always be prepared afresh.

Tin Prussiate (Sn_2FeCy_6) can scarcely be called a mordant, and is found very useful in the preparation of steam prussiate blue colours in printing, as the presence of tin gives a brighter shade than if no tin is employed. It is sometimes found in commerce, and is generally known as tin pulp or prussiate of tin pulp.

Stannic Chloride ($SnCl_4$) is obtained by oxidation of the stannous salt by different methods, such as treating a tin salt solution with chlorine gas, or with chlorate of potash and hydrochloric acid, or by treating tin crystals with nitric acid and a small amount of water. The method of oxidation by means of a chlorate is a very convenient one, the proportion being

337 grs. tin crystals.
500 ,, hydrochloric acid 20°Tw.
58 ,, potassium chlorate.

The tin crystals and the acid are first mixed together, if necessary, with the addition of a little water, the whole is then gently heated and the chlorate added in small portions at a time, an excess of chlorate being shown by the yellow colour of the solution, which will otherwise be colourless.

The commercial stannic chloride is generally a crystalline product containing 5 molecules water,

$$SnCl_4 + 5H_2O.$$

and should be tested for tin by gravimetric analysis.

Stannic chloride is employed in printing, but not to a very great extent; it is used for brightening, or what is generally known as *Cutting*, in the madder styles; the commercial product used for this purpose is known as oxymuriate of tin or pink cutting liquor; and is very often prepared as follows:—

Place

100 grs. tin crystals	1 lb.

in an earthenware or enamelled iron vessel, then add in small portions at a time, stirring well,

140 to 150 grs. nitric acid of 1·31 sp. gr.... about	1½lbs.

The product is afterwards diluted with the necessary amount of water.

Stannic salt solutions are also prepared in other ways, such as by dissolving tin in a certain proportion of nitric and hydrochloric acid, and many preparations used under different names are more of interest to the wool dyers.

Pink Salt was at one time a very popular product for the calico printer, but is not much used now. It is a double salt of stannic and ammonium chlorides:

$$SnCl_4 + 2(NH_4Cl).$$

When heating a diluted solution of this double salt a decomposition takes place, the hydrated stannic oxide being formed.

Stannate of Soda (Na_2SnO_3).—This product, also known as preparing salt, is manufactured on a large scale by several processes, some utilising metallic tin, and others employing the scraps or cuttings of tinned iron now so largely produced in establishments engaged in the tinning of preserved milk, fruits, meat, and other comestibles.

Tin, when fused with caustic and nitrate of soda, is converted into the stannate, and this is the method generally followed on a large scale.

The commercial article forms a dry white mass, which contains more or less stannate of soda, as it is, in many cases, mixed with carbonate of soda, or even common salt. When freshly made the salt dissolves completely in hot water, but by standing, a decomposition takes place, and a certain amount becomes insoluble. Therefore, in testing commercial samples it is necessary not only to estimate the amount of metallic tin or oxide contained in the same, but to ascertain at the same time the amount of insoluble product. Some qualities of commercial stannate of soda contain about 24 per cent. metallic tin.

Stannate of soda is employed in cotton dyeing pretty largely as a mordant for producing stannic acid on the fibre, the cloth being first passed through the stannate of soda and afterwards through weak sulphuric acid, which by combining with the soda, will precipitate the stannic acid on the fibre.

$$Na_2SnO_3 + H_2SO_4 + H_2O = Na_2SO_4 + Sn(OH)_4$$

The same principle is followed in preparing cloth which is afterwards printed with steam colours, and it is for this reason that the salt has been called preparing salt.

Commercial stannate of soda samples should be tested for the amount of stannic oxide (SnO_2), or of metallic tin they contain, also the nature of adulteration should be ascertained.

A rapid and yet practical method of estimation of tin mordants is to dissolve a sample in water, adding hydrochloric acid until it shows a slight excess, and then to precipitate the metallic tin by means of zinc. The metallic tin can be then collected, washed, and weighed.

COPPER MORDANTS.

Copper compounds are used only in a few cases as mordants in the strict sense of the word; they are oftener employed on account of their oxidising powers. The most common of the copper salts is the

Sulphate of Copper (Blue Vitriol: $CuSO_4 + 5H_2O$), which is found in commerce generally in the form of large blue crystals of the tricline system. It is produced by treating copper with weak sulphuric acid, and then evaporating the liquor and allowing the salt to crystallise out.

It is sometimes produced as a bye-product of other industries.

Its principal employment is in black dyeing with logwood, in which it is connected either with bichrome or with iron mordants. It is also employed in the manufacture of other products or mordants for printing, as in sulphide of copper paste.

In testing the commercial product, after estimating the amount of water of crystallisation, copper is estimated gravimetrically, or even by the electrolytical method, as for other soluble copper salts. The commercial sulphate should be also tested for iron.

Chloride of Copper ($CuCl_2 + 3H_2O$) is a product which is found in commerce in small crystalline needles, or as a liquid at about 60° Tw., and is useful in several processes of oxidation; for instance, in the manufacture of methyl violets and in the oxidation of cutch colours.

It is obtained by dissolving metallic copper in hydrochloric acid.

The commercial product should be tested for iron or sulphuric acid, and the amount of copper should be determined.

Nitrate of Copper ($Cu(NO_3)_2$), which is obtained by dissolving copper with nitric acid, crystallises either with three or five molecules of water. It is only sparingly used in dyeing and printing of cotton.

Acetate of Copper ($Cu(C_2H_3O_2)_2 + H_2O$) can be produced in several ways, either by the double decomposition of the copper sulphate with the acetate of lead, or by dissolving the hydrate or carbonate in acetic acid. The product is very soluble in water.

Verdigris ($Cu_2O(C_2H_3O_2)_2 + 6H_2O$) is a basic copper acetate, the above formula illustrating one of the best known of these basic products.

Copper Sulphide (CuS).—Although not so much used now as formerly, this is still employed in printing for the development of aniline black, being produced by the double decomposition of the sulphate of copper with sodium sulphide, and then utilised in the form of a paste.

LEAD MORDANTS.

Acetate of Lead ($Pb(C_2H_3O_2)_2 + 3H_2O$) is a very useful product in the hands of the calico printer, because it not only does good service in preparing acetates, but also serves at the same time as a real mordant in the formation of chrome yellows and oranges, by being first printed on cloth which is afterwards dyed or raised in the bichromate bath. The commercial product is obtained on a large scale generally in works where acetic acid is produced by the distillation of wood, or decomposition of the acetates of lime, and according as a more or less pure acid has been used in the treatment of lead compounds, for which litharge is generally employed, a more or less pure product is obtained.

In commerce two qualities are distinguished, generally known as brown or white sugar of lead.

In testing commercial samples the amount of metallic lead or lead oxide (PbO.) should be ascertained, in a pure product the latter averages about 58·8 per cent., while the water amounts to about 14 per cent. For the lower qualities the amount of insoluble should be estimated. With impure products no very bright colours can be obtained; and of course the amount of acetic acid is of importance if the product is employed in the preparation of acetates.

Basic Acetate of Lead ($Pb(C_2H_3O)_2 + PbO$) is generally produced by heating together, to the boiling point, equal parts of normal lead acetate, water, and litharge, leaving the mixture to settle, and using the clear filtered liquor. This is employed in mordanting cotton for chrome oranges, and even deep yellows. As it absorbs carbonic acid from the atmosphere it should be always freshly prepared.

Nitrate of Lead ($Pb(NO_3)_2$) is obtained by treating metallic lead, or lead oxides, by means of nitric acid, and is found in commerce in crystallised form. The following proportions are found useful for preparing this mordant in solution.

100	grs.	Litharge	10 lbs.
75	,,	Nitric acid 50° Tw.	7½ ,,
75	,,	Water	7½ ,,

Are mixed together, stirred occasionally, and left to react for several days, then filtered, and the clear liquor made up to about 15° Tw. In order to prevent any excess of nitric acid a small amount of litharge is shaken up with the liquor and left to settle.

The nitrate of lead is used in the production of chrome yellows on cotton, and also for the preparation of nitrate of alumina, &c., finding extensive application in printing.

The pure product contains about 67·5 per cent. oxide of lead.

Peroxide of Lead (PbO_2) is a powerful oxidiser, and is sometimes used in indigo discharging.

The lead mordants are tested generally for the amount of $Pb\,O.$ they contain, by gravimetric analysis.

They can also be tested volumetrically by precipitating the lead out of the water solution, by means of carbonate of soda, and dissolving the filtered and washed carbonate by means of normal nitric acid solution, and titrating back the excess of nitric solution used.

MANGANESE MORDANTS.

CHLORIDE OF MANGANESE ($MnCl_2$).—This is obtained as a bye-product in the manufacture of chlorine, and is utilised in the form of a concentrated solution; the salt crystallises with four molecules water, is of a rose red colour, and is very hygroscopic. The employment of the manganese chloride is limited to the product of brown of great fastness on cotton. When heated with alkalis the chloride is decomposed, and hydrate of manganese is formed,

$$MnCl_2 + 2NaOH = 2NaCl + Mn(OH)_2.$$

The hydrate of manganese is formed on the fibre by mordanting the cloth with manganese chloride and passing in a soda bath; the hydrate in contact with air is peroxidised, and by passing afterwards in a bath containing bleaching powder a brown is produced, known as manganese brown or bronze. This colour has the property of being destroyed by reducing agents, and this reaction is utilized in forming white patterns on brown or bronze grounds, by applying a thickened solution of stannous chloride, which will discharge the colour where it is printed on the cloth.

Manganese chloride is also employed in the preparation of cutch colours, and in the production of steam manganese browns in calico printing.

SULPHATE OF MANGANESE ($MnSO_4$), is found in commerce generally in the form of a dry powder, not completely soluble in water. It is also sometimes found crystallised with seven molecules water. It is employed for the same purpose as the chloride, and also for the preparation of *acetate of manganese* in proportion of one part of the pure manganese product and about 1½ parts of acetate of lead.

Permanganate of Potash ($KMnO_4$) would be even a more useful product than it now is if it could be obtained at a low price, as it is a powerful oxidiser. The commercial product is generally found in fine metallic looking crystals, readily soluble in water, with a violet red colour. The impure qualities do not dissolve completely in water, and contain from 50 to 70 per cent. of the pure product.

Commercial samples should be tested for amount of $KMnO_4$, by the volumetric methods, using, for instance, a standard oxalic acid solution.

Permanganate of soda is also found in commerce, but generally in a very impure state.

ZINC MORDANTS.

Zinc salts are very little used as mordants. Of the commercial products the most important are

Chloride of Zinc ($ZnCl_2$), which is found either in the form of strong solution, showing about 90° Tw., or in the dry state. It is principally produced on a large scale by dissolving metallic zinc in hydrochloric acid, and then either concentrating to a certain degree, or evaporating to dryness. When dry the white mass is very hygroscopic, and therefore must not be exposed to air.

Chloride of zinc is mostly used as an antiseptic in the preparation of mixtures for sizing cotton yarn before weaving, and it prevents the fermentation of the starchy substance, at the same time giving weight to cotton by attracting water from the atmosphere. It is pretty extensively used in the manufacture of some aniline colours.

The commercial product should be tested for the amount of metallic zinc it contains, and should be free from iron.

Sulphate of Zinc ($ZnSO_4 + 7H_2O$), also called zinc vitriol, is found in a crystallised form in commerce, sometimes of very great purity. It is extensively used, like the chloride, for the manufacture of coal tar colours, as zinc chloride gives double salts with several aniline colours, which can then be easily salted out and brought into commerce in a dry state.

By treating a solution of zinc sulphate with an insufficient amount to precipitate the whole oxide, a product is obtained which will act as reserve under alizarin pink.

ACETATE OF ZINC is produced by double decomposition from sulphate of zinc and lead acetate, or by dissolving precipitated zinc hydrate or carbonate in acetic acid. It has been recommended as a substitute of tartar emetic for the fixation of tannic acid aniline colours after steaming, but it has not found very extensive application for this purpose, as patterns which contain alizarin reds do not come out so well as when the tartar emetic is used.

SULPHIDE OF ZINC (ZnS) has been recommended and used for fixing alizarin blue, and some other coal tar colours, but has not hitherto been employed to any great extent.

ARSENIC MORDANTS.

ARSENIOUS ACID (As_2O_3) is still employed in the fixation of some aniline colours, especially the bright greenish shades of aniline blue, in spite of its poisonous character.

The commercial product forms a white powder, or sometimes a fused mass; the powder is often adulterated with sulphate of barium or gypsum, which can be easily detected by igniting a small sample and weighing the ash which remains behind, or by dissolving in caustic soda, where the adulterant is insoluble. Its principal employment in printing is in the preparation of steam colours, being either dissolved in glycerine or in the form of *Arsenite of Soda,* dissolved either by means of soda crystals or in some cases of borax. The arsenite is used also as a fixing liquor for alizarin purples, and sometimes a reserve under aniline black. It is also found in commerce in powder form, often adulterated by means of common salt, and consequently containing a variable amount of the sodium arsenite Na_3AsO_3; sometimes also the salt corresponds to the formula Na_2HAsO_3, and containing about 44 per cent. arsenic or 58 per cent As_2O_3.

In testing, the presence of chlorine, and consequently of common salt, is detected by means of nitrate of silver in a solution of the product in weak nitric acid. The amount of arsenious acid is estimated by volumetric analysis by means of iodine.

ANTIMONY MORDANTS.

Tartar Emetic ($2KSbOC_4H_4O_6 + H_2O$) is very largely employed in calico printing for the fixation of tannic acid steam colours, and is also used in dyeing for the fixation of tannic acid on cotton, which is afterwards dyed in aniline colours. Antimony is, as yet, the best agent for the fixation of tannic acid on the fibre, the lakes thus produced with the basic aniline colours being faster to soap than those produced by other metallic tannates. The employment of tartar emetic for the purpose of fixing aniline colours in calico printing by the tannic acid process is due to Thomas Brooke, of Manchester.

In its pure form, tartar emetic forms a clear crystallised product, either octahedral or tetrahedral; when exposed to air, however, it loses a certain amount of water of crystallisation, and the crystals lose a certain amount of transparency, and become pulverulent and friable. The commercial article is generally met in the form of crystalline powder, sometimes very largely adulterated with sulphate of potash, or mixed with the oxalate. Pure tartar emetic contains about 43 per cent. SbO or 35.5 per cent. metallic antimony. Tartar emetic is soluble in two parts boiling water, and 14 to 15 parts cold water.

When employed in the bath through which the cloth is passed which has been printed with the aniline colours and steamed, it is found that after awhile, and when many pieces have been passed through, the bath is, if not rendered useless, to a great extent weakened by the tartaric acid, which is formed by the decomposition of tartar emetic by means of tannic acid, which precipitates the insoluble tannate on the fibre; for this reason it has been found necessary in working tartar emetic baths to add a certain amount of chalk, which forms a basic antimony salt, which is, however, rendered again soluble by the tartaric acid or acid tartrate of potassium formed by the passage through the same bath of other lots of cloth.

Tartar emetic has a brightening effect on steam alizarin red, which is printed at the same time with the other aniline colours, and which after steaming are passed through the tartar emetic bath; this, according to Lauber, is due not so much to the antimony as to the action of the free tartaric acid or acid tartrate, in the same way as the tin cutting baths, since a bath neutralized with chalk has not the same brightening influence. It is not only the amount of antimony which is of importance in good qualities of tartar emetic, but the product must be free from iron or other metallic compounds, such as copper, because if contaminated with them it will spoil the beauty of the shades obtained by the grey colouration added by the tannate of iron or copper, which would be formed in passing the piece printed with the tannic acid colours through the tartar emetic solution containing iron; and it must be tested for this impurity by acidifying a solution of the tartar emetic sample with acetic acid, and then adding a solution of red prussiate of potash, when no precipitation must take place. It could also be tested in a more direct way by adding a diluted solution of tannic acid to a solution of tartar emetic, and judging by the colouration of the precipitate formed. The amount of antimony is estimated by means of iodine, and the adulteration with sulphate of potash must also be determined.

OXALATE OF ANTIMONY AND POTASH ($Sb(C_2O_4K)_4 + 6H_2O$.)—This product has been employed a long time in dyeing and printing under different names, or as an adulterant of tartar emetic, and it is only through the experiments of Noelting that it has been recommended on its own merits as a substitute for the tartar emetic.

It is, as seen from the formula, a double salt of antimony and potash, and it contains 28·67 per cent. of oxide of antimony, or 19·97 per cent. metallic antimony, while, according to Gerland, the formula of the oxalate is $Sb_2K_6.6C_2O_4 + 2\frac{1}{2}H_2O$, and contains 21·3 per cent. antimony. In comparison to the selling prices it is a cheaper product than tartar emetic, even in proportion to the respective amount of antimony, as oxalic acid is much cheaper than tartaric acid. The commercial article is sold either as a powder, or in the form of crystals similar to those of oxalic acid, which in a small amount of water give a clear solution, but when diluted (in proportion to the strength generally used in practice in the preparation of the fixing bath), a partial dissociation takes place, and the bath becomes turbid by the formation of a basic oxalate, while a more acid product remains in solution.

The oxalate of antimony has been employed successfully in some printworks, and any failure in its successful employment has been ascribed to the employment of too concentrated baths. But it is a matter that every practical man can test for himself, which is cheapest and best for him to use, the tartar emetic or the oxalate.

A solution containing 5 grs. oxalate of antimony and potash per litre of water is sufficiently strong for the fixation of tannic acid colours, while too strong solutions, even those containing 10 or 20 grs. oxalate per litre, do not act so well.

The oxalate dissociates more readily than the tartar emetic, and the acid oxalate which remains in solution does not assert so strong a dissolving action on the antimony tannate as the acid tartrate of potash.

The estimation of the amount of antimony in the oxalate can be effected by the ordinary method with iodine, or, as recommended by Casthelaz and Bruère, by treating a sample with sulphuric acid to decompose to oxalic acid, then neutralising with ammonia; to redissolve in hydrochloric acid, and titrate with permanganate of potash.

Fluoride of Antimony is a product of recent introduction, and is sold either in solution or as a crystalline powder, the latter containing 39 per cent. metallic antimony. It seems to behave as well as tartar emetic.

Oxymuriate of Antimony.—A product under this name has been many years in use in dye and print works, especially in America, principally for the fixation of tannic acid on cloth or yarn, previously mordanted with tannic or sumach solutions. The product is sold as a concentrated solution, which is obtained by dissolving metallic antimony in a mixture of nitric and hydrochloric acid, and before use diluting with water, when a milky solution is produced which is made up to a certain degree Tw., and used as a fixing bath, or neutralised to a certain extent with soda before use.

Antimony Alkaline Mordant.—The oxide of antimony dissolves in a solution of glycerine and caustic-soda lye, and yields an alkaline mordant which may be found useful for several purposes in dyeing or printing, for fixing antimony oxide on the fibre.

It has also been recommended as a substitute for tartar emetic, but as yet has only been tried on a small scale; the presence of an alkali will, however, be a drawback in its employment, since it will act injuriously towards the colours.

Other Antimony Mordants have been recommended as substitutes for tartar emetic, among which the chloride previously neutralised with soda crystals, and even the precipitated hydrate of antimony, which has been recommended to be used in printing along with a certain amount of oxalate of ammonia, and thus do away with the following antimony bath, but so far no good results have been obtained on the large scale with these proposed new mordants.

VANADIUM COMPOUNDS.

Vanadium is the most powerful oxygen carrier which has been discovered for the oxidation of aniline into aniline black, as it has been proved that one part of vanadium was sufficient for 100,000 parts of thickened colour, and this explains why, even at such high price, the vanadium compounds can still be cheaply employed in printing.

VANADIATE OF AMMONIA (NH_4VO_3).—The ammonia salt of metavanadic acid is the one generally found in commerce, and is either used as such or converted into *Vanadium Chloride* by reduction with glycerine and hydrochloric acid.

The ammon vanadiate is a white powder not easily soluble in water—in the proportion of about 1 to 100.

The slags obtained, as bye-product, in the dephosphorisation of iron, by the Thomas Gilchrist process, contain a certain amount of vanadium, and have been employed in preparing vanadium solutions for the fixing of aniline black, in about the following proportions:—

100 grs. of the slag are dissolved at about 90°C. in
200 ,, hydrochloric acid and
200 ,, water, and the solution filtered, and then made up to
1 litre, or more, according to the amount of vanadium contained in the slag.

In testing samples of vanadium preparations the best method to follow is a practical printing trial, but vanadiates can be tested by titration with a standard solution of the double sulphate of iron and ammonia, containing 7 grammes of the pure salt, and 5 to 10cc. sulphuric acid in 1 litre water; when 1cc. of this solution will correspond to ·00207 vanadiate of ammonia, or ·00163 anhydrous vanadic acid, red prussiate of potash is employed as an indicator, the iron standard solution being added to the vanadiate solution until a drop placed on a white porcelain plate gives a blue spot with the red prussiate solution.

CERIUM SALTS

Have also been recommended, and to a small extent used in the preparation of aniline black colours, but as they do not offer any advantages over the vanadium salts they have almost been given up.

THE ACID SULPHATE OF CERIUM ($Ce(SO_4)_2H_2SO_4$) is the product which has been principally employed, and is obtained from Cerit by treatment with sulphuric acid. It is found in commerce in solution of 30° Tw., and can be employed in an equal proportion of weight instead of the sulphide of copper paste.

DUNGING MATERIALS

COW-DUNG is yet employed to a certain extent, notwithstanding the fact that substitutes are so plentifully met with in the market, and some practical men assert that they cannot obtain so good results as with the cow-dung. It is not yet satisfactorily explained in which way the cow-dung reacts in the process of fixing or dunging of the mordants, no doubt the phosphate of soda and carbonate of ammonia which are generally met in cow-dung, assert by themselves a fixing action, but the organic substances also take part in the cleansing and fixing process; in fact, an aqueous extract of the dung contains a mixture of organic substances, albuminoids, &c., which are capable of forming precipitates with metallic oxides. Cow-dung is generally used in the proportion of one part dung in about 50 parts of water, to which sometimes a certain amount of chalk is added, especially for heavy patterns, and when acid colours have been printed.

No chemical test will give any indication concerning the property of the cow-dung, therefore the only reliable method is to test by a practical dunging trial, the cloth being afterwards dyed with alizarin.

ARSENIATE OF SODA (Na_3AsO_4).—A very useful product for dunging purposes, coming generally into commerce in the form of a powder or in small fused lumps, and easily soluble in hot water. It is sometimes also sold in solution under the name of dunging or fixing liquor; in this case, however, very often accompanied by an excess of alkali, which acts injuriously in the fixation of mordants. The commercial products vary considerably in the amount of arsenic acid they contain, ranging to 55 or 60 per cent.

In testing commercial samples, the arsenic acid is estimated by gravimetric method, by precipitation with magnesium mixture, and weighing the ignited arseniate of magnesia.

BINARSENIATE OF SODA ($NaH_2AsO_4 + H_2O$) is also employed for dunging purposes, the commercial products possessing variable amounts of arsenic acid, and being distinguished according to the amount of the latter as 50 or 60 per cent., &c. The testing of commercial samples is effected in the same way as for the neutral arseniate.

The commercial products are found either in the form of small white lumps, sometimes also crystallised, having the above formula, but mixed with a product containing less arsenic acid and more water of crystallisation, and having the formula $NaH.AsO_4 + 12H_2O$.

A quicker method of estimation of commercial value of arseniates is by titration with iodine. The arseniate is reduced by means of hydrochloric acid and an excess of bisulphite of soda, with which the solution of the sample is left in contact for several hours, and after expelling any free sulphurous acid by heating, without reaching the boiling point, it is titrated by means of a standard solution of iodine.

PHOSPHATE OF SODA ($Na_2HPO_4 + 12H_2O$) is a very good dunging or fixing material, but is not so largely used as the arseniate, as the latter is cheaper.

In preparing a dunging bath with this material, 40 to 50 grs. of phosphate are used per 10 litres of water, to which is added 8 grs. of chalk, the temperature is then raised to about 65° C. and the cloth passed for one minute through this bath.

In testing commercial samples the amount of phosphoric acid must be estimated.

Silicate of Soda ($Na_2Si_4O_9$).—This product, which is generally found in commerce as a thick syrup, is not much used in England for dunging purposes, but is more largely employed on the Continent. For alumina mordants it is not to be recommended, as it is very often accompanied by free alkali, but for iron mordants it can be safely used.

Carbonate of Ammonium has been often recommended as a dunging material, and would be largely employed but for its high price.

Of other dunging materials which have been used must be mentioned Chalk, which has already been described among the white pigments.

Bran is also used sometimes on the Continent for dunging purposes, but not very often.

ASTRINGENTS OR TANNING MATERIALS.

Under this class are comprised several products of the vegetable kingdom, which contain, as active principle, tannin or tannic acid, which, if not identical in the different plants, offers in many instances the same principal characteristics of forming insoluble compounds with some metallic oxides. These astringents are sometimes distinguished into two classes, viz., the blue tannins and the green tanning products, according as their extracts yield blueish or greenish precipitates with iron. Of the green varieties cutch or catechu is the most important. This is more a colouring matter than a mordant, and has therefore already been treated among the natural organic dye stuffs. Of the others the principal employed are the following:—

SUMAC OR SUMACH.—This is one of the most important products of this class, if not the one most largely employed in tinctorial arts, its application having considerably increased since the introduction of coal tar colours in dyeing and printing. It comes of different quality and price into commerce, being mostly the ground dried leaves or young twigs of different plants of the family of *therebintaceæ*, genus *rhus*, the most important varieties of which are Sicily sumach (*rhus coriaria*), Tyrol or Venetian sumach (*rhus cotinus*), French sumachs consisting of varieties of *coriaria myrtifolia*, and Algerian sumach (*rhus pentaphylla*). The North American varieties are the *rhus glabra* or white sumach, the *rhus canadensis* and *rhus capallina* or black sumach.

In commerce the varieties are generally distinguished from each other by the name of the places from which they are derived, and besides some of the names mentioned above, the Spanish or Malaga and Portuguese sumachs are known, while the American varieties are distinguished also under the name of Virginia or Carolina sumachs.

Of the different varieties the Sicily sumach is the most appreciated, not only on account of the larger amount of tannic acid it yields, which in some cases has been found to average and even to exceed from 15 to 20 per cent. but also on account of its containing only a small amount of colouring matter, and not acting injuriously in the dyeing of delicate shades.

Commercial varieties are very often largely adulterated, and contain consequently a smaller amount of tannic acid.

SUMACH EXTRACTS are manufactured in large quantities and of very good quality by the works engaged in the manufacture of dyewood extracts, and by the same processes of evaporation, principally in the vacuum apparatus. They offer great advantages to the calico printer, because the product is quite ready for use, and is sold of regular strength. The extracts of sumach can be safely employed in all cases when no very delicate shades are required; but when very pure colours are wanted, tannic acid must be used instead.

The methods of estimation of the commercial value of sumach or the extracts will be mentioned later on.

GALLS do not occupy such an important place as formerly in dyeing, but for printing they constitute a very valuable product, being employed in the form of extracts in the fixation of different colours.

They form also a very important material for the manufacture of commercial tannic acids.

Several varieties of galls, or *nut galls*, are met with in commerce, among which the principal are the following:—

Aleppo or Turkish galls, China galls, French and Piedmontese galls, &c.

They are generally globular excrescences produced by an insect on the leaves or young twigs of different varieties of oak, principally on the *quercus infectoria*.

The commercial products vary pretty considerably in price and quality in proportion to the tannic acid contained in them; for instance, Aleppo galls contain from 55 to 77 per cent., while others of inferior quality, such as Istria galls, only contain 24 per cent. tannin.

GALLS EXTRACT is also met with in commerce, and is produced by the ordinary methods.

VALONIA NUTS are the acorn cups of a variety of oak, the *quercus aegilope*, and are also known as Levant nutgalls, and form a pretty important article of commerce.

DIVI-DIVI is one of the cheapest of the astringents, and is an important commercial article on account of the comparatively large amount of tannin it contains; it is in this respect stronger than sumach, but it has the drawback of containing a certain amount of colouring matter, which makes it unfit for many purposes. The commercial product is formed of the pods of the *caesalpina coriaria*, a small tree growing in different parts of South America.

MYROBOLAMS is rather a popular product among some dyers, especially those engaged in the dyeing of black Italian cloth. In commerce it is found either ground, or in its original form of pale buff-coloured dry pulp of the fruit of *terminalia caebula*, which very much resemble dried plums. Mirobolams is stronger than sumach, and has displaced the latter for many purposes.

The commercial article is very often adulterated with poor or even spent sumach, and also with divi-divi, which adulterations can easily be detected by means of a lens.

TANNIC ACID ($C_{14}H_{10}O_9$).—Although formerly only employed in medicine, pure tannic acid is now produced on a very extensive scale, and finds large employment in dyeing, and especially in calico printing, when delicate shades are to be produced.

Commercial tannic acids are generally produced by extracting Chinese galls by means of a mixture of ether, alcohol, and water. In the watery layer is found the tannic acid, while the ether will contain the colouring matters, fatty resinous substances.

Tannic acid is sold either in the form of powder, or granulated, or in the form of needles, very often of great purity.

Tannin is an acid which forms combinations with metallic oxides, some of which are insoluble and white, and others deeply coloured. It is for its property of forming insoluble lakes, or tannates, that tannic acid is employed in dyeing and printing.

In the fixation of basic coal tar colours, tannic acid has been found most valuable, and, in fact, could not be dispensed with in the modern industry of calico printing. Although tannic acid gives insoluble tannates with many of the aniline colour bases, the combinations when formed on the fibre do not stand the action of soap, and it is necessary to use at the same time a metallic oxide, which, by combining with the coloured lake, imparts to it the property of standing much better the action of soap. It is not yet explained in which way the metallic oxide really acts, but it is very likely that a double compound is formed in which a double tannate of the metallic oxide with the colour base is produced. In the employment of tannic acids in dyeing and printing care must be taken, in dissolving the product, not to use too high a temperature, or the shades produced will not turn out so pure. Tannic acid is very soluble in water, and consequently not much boiling is required in preparing the solutions.

The manufacture of tannic acids is almost completely confined to Germany.

Gallic Acid is found in some astringents along with tannic acid, and is even met with in small quantity in commercial tannins. It has no value in the fixation of colours on fabric, but is the raw material for the manufacture of pyrogallic acid, which serves for the preparation of the dyestuff galleine, and afterwards coerulein.

Estimation of Commercial Value of Tannins and Astringent Materials. — The active principle of all these products being tannic acid, the value of the commercial articles will depend upon the amount of tannic acid they contain. Although many methods have been recommended for the estimation of tannic acid, there are none which can be considered thoroughly satisfactory; the Löwenthal method may be considered the best, and will give correct results if the tannic acids of commerce are tested, but even this process becomes unreliable when it is a question of extracts or decoctions of the raw material. These extracts will contain, in addition to the tannin, a certain amount of organic substances, which will act in the titration process on the permanganate.

Löwenthal's method relies on the titration of tannic acid by means of permanganate of potash, indigo carmine being used as an indicator. The tannic acid is then precipitated out of a portion of the solution by means of glue or gelatine and salt solution, and the liquor titrated again by means of permanganate of potash, the difference between the two titrations indicating the amount of tannic acid.

This method may be considered good when working on pretty pure materials, and can be found very useful as a comparative one by testing the samples against a standard tannic acid of known quality.

The method of testing by dyeing and printing is often the more reliable, since it indicates at once the relative value of the different materials for the purposes for which they are used.

The testings are generally performed by dyeing, with respective samples, cotton cloth which has been either mordanted all over with acetate of iron, or on which the same mordants have been printed on in stripes similar to those used in the madder styles, viz., alumina and iron, or mixtures of both.

Another method consists in mordanting with the corresponding amounts of the samples, fixing with tartar emetic, and afterwards dyeing with methyl or malachite green in excess, and, after washing and soaping, the dyed patterns are compared. If the amount of the samples has been calculated in proportion to their respective price, the sample which has produced the deepest shade will be the cheapest.

In all cases the tests should be made by the same methods for which they are employed in practice. For instance, if a commercial tannic acid is to be employed in the preparation of steam colours, it should be tried for this purpose in comparison with a standard sample, and in proportion to their respective prices.

SOAPS.

Under the name of soaps are understood a great variety of combinations of fatty acids with metallic oxides, which are soluble or insoluble according to the base employed. For instance, the soaps of heavy metallic oxides and alkaline earths are insoluble, while those obtained with alkalis are soluble in water. The soluble soaps are those employed in practice, while the insoluble compounds are sometimes produced on the fibre, and serve really as mordants for the fixation of colouring matters. The soluble soaps are considered as detergents or cleansers, or even brightening agents, and find extensive employment in cotton dyeing, and especially in calico printing, for which purpose they are found invaluable. The soluble soaps are divided into soft or hard soaps; the first being derivatives of potash, and scarcely ever employed in printing, while the hard or soda soaps are generally utilized.

The manufacture of soaps is carried on to an enormous extent, and the commercial products vary considerably in point of price and usefulness. The animal and vegetable fats or oils are generally glycerides, which in the process of saponification are split up into the fatty acids which combine with the alkali to form the soap, or really to produce a salt, while the glycerine remains free. According to the fatty substance employed in the manufacture, soaps of different qualities are produced, which are not always suitable for dyeing or printing; the process of manufacture is also of great influence on the quality of the soap produced.

For calico printing and dyeing the soaps derived from tallow, palm oil or olive oil are generally employed; the latter being sometimes preferred for turkey red dyeing. The soaps produced from the liquid fatty acid (oleic acid), the by-product of the stearine candle manufacture, are also found in commerce in large quantities, and consist mostly of oleate of soda, while the soaps produced from tallow consist of a larger proportion of stearate and a smaller amount of oleate of soda.

There are three principal methods of manufacture of soaps: the cold process; the boiling method, accompanied or not by the salting out; and the treatment under pressure.

A good soap for the calico printer and dyer must possess two important properties—it must be as neutral as possible, and thoroughly saponified; this second quality is of great importance, since two soaps may contain exactly the same amount of alkali, and yet one will not act as well as the other if it has not been well boiled or saponified, since in this case it will not consist entirely of the combination of the fatty acid with the soda, but will contain also undecomposed fat and alkali.

The analysis of soap is not a sure indication of its usefulness in practice, although it gives a good idea of its commercial value. In testing soap the moisture is first of all ascertained by drying a sample, and the amount of fatty acid and soda is then estimated.

Soaps are very often largely adulterated with insoluble substances, which must be estimated. Silicate of soda and resin are commonly employed for the adulteration of soap.

The free alkali in soap must also be estimated by extracting a sample with absolute alcohol, and determining the amount of alkali in the extract.

As said before, an analysis of soap is not a sure indication of the way it will react in practice, and therefore a practical trial must always be made in testing samples of soap to ascertain their suitability for printing and dyeing, or for clearing the whites and brightening the colours after printing, since an alkaline and badly saponified soap will strip out some of the colours and not effect the brightening of the shades.

The theory of the employment of soap in the dyeing and printing of cotton is not yet fully explained; soap acts as a detergent, not only mechanically, but by its power of solubility, by dissolving some of the substances while forming emulsions with fats or fatty substance. In many cases soap enters really in the formation of coloured lake, and this explains the brightening effected by the soaping processes.

Of the commercial articles the Marseilles soap or olive oil soaps are preferred by some practical men for turkey red dyeing and printing. These are obtained from olive oil by boiling and salting out processes, and are largely produced in the South of France and in Italy.

A good olive oil soap will show about the following composition:

Water	30 to 35 per cent.
Fatty acid	60 to 61 ,,
Soda	5 to 6 ,,

The value of the neutrality and of a thorough saponification of soap is fully recognised by practical men, and several methods have been tried for the manufacture or treatment of the soaps to be used by calico printers, such as melting the soap before use, or boiling the same with a certain amount of fat or fatty acid to neutralize any free alkali present. This is, however, not a method greatly to be recommended, since it is apt to give a greasy product, acting, in a different way, more injuriously than before. A good and sufficiently long boiling of the soap in manufacturing, and a good mixing when salting out, will give a good product, since any free alkali will be dissolved in the salt liquor along with glycerine, and a second washing of the separated soap with hot salt water will, if well stirred, remove any excess of alkali still left in the product.

Another method for producing a neutral soap is to add, after the boiling and before cooling the liquid soap, a certain amount of an ammonia salt, which, by being decomposed by the free alkali, renders the latter completely innocuous, while the ammonia produced at the same time either escapes or will not act as injuriously as the soda.

Manufacture of Soap by Boiling under Pressure. By treating oleic acid with the necessary amount of caustic lye, in a closed boiler under pressure, the saponification is effected completely in four or five hours, and the product can then be employed at once in printing, for the clearing of the whites by soaping.

OILS.

Olive Oil finds a pretty extensive application in the preparation of many printing colours, to which it is added in small quantities, but is a very important raw material for soap making, and finds also employment as a true mordanting material in dyeing and printing of cotton.

Olive oil consists of two fatty bodies, the trioleïne $C_3H_5(OC_{18}H_{33}O)_3$, or glyceride of the liquid *oleic acid*, $C_{17}H_{33}COOH$., and the *tripolmitin*, $C_3H_5(OC_{16}H_{31}O)_3$, or glyceride of palmitic acid, a solid fatty acid. A variety of olive oil, the *gallipoli* oil (*Huile Tournante*), also called emulsive oil, was at one time, and is still to a certain extent, a very important material in the production of turkey reds. It is of an acid or rancid character, and comes into commerce of different quality. It forms pretty permanent emulsions with carbonate of soda or potash, and it is tested by this property; a sample of the oil is mixed with potash or soda lye, and left standing for about an hour; if the oil is suitable for the old process of turkey red dyeing, the white emulsion is still apparent, otherwise the oil separates out very soon.

The emulsive oils contain a certain amount of free fatty acid, and they are produced from the ordinary olive oils by different processes.

The olive oils generally are pretty largely adulterated with cheaper oils, such as cotton seed, poppy oil, &c., and the adulteration is rather difficult to detect.

Olive Seed Oil.—After the oil has been extracted from the olives, by pressing out, the residues, which consist of the kernels and the pulp of the fruit, still contain a certain amount of an inferior oil, which is extracted by means of bisulphite of carbon, and comes into commerce in large quantities, generally of a greenish colour, and finds mostly employment in the manufacture of green olive oil soaps.

Castor Oil is extracted by mechanical means from the berries of the *Ricinus* plant, and is composed of the glyceride ($C_3H_5(OC_{18}H_{33}O_2)_3$) of ricinoleïc acid ($C_{18}H_{33}O_2OH$). At one time it was only employed in medicine, but it is now very largely utilised in the manufacture of oil mordants for alizarin dyeing and printing.

Other oils and fats have been used in the preparation of cotton goods for turkey red or alizarin dyeing, but only olive or castor oils are regularly and successfully employed.

The Oleic Acid, sometimes called olein, of the stearin candle manufacture finds an extensive employment in soap making, and has been also used in the manufacture of prepared oils for alizarin dyeing, alone, or as an adulterant of the products of castor oil, but the preparations containing this modified oleic acid often give a very peculiar smell to the goods, which is sometimes objectionable.

Linseed Oil has also been employed as a mordant for cotton, and on account of its low price might find some employment for purposes in which the peculiar smell it imparts to the goods is not an objection to its use.

PREPARED OIL MORDANTS.

The manufacture of prepared oils for alizarin dyeing and printing has attained a very important development. The preparations come into commerce under different names, such as alizarin oil, turkey red oil, oleine, sulphated oil, &c., and are mostly derivatives of castor oil. In the majority of cases they are produced by treatment with sulphuric acid.

Many dye or printworks prepare their own alizarin oils, as the process is a very simple one, consisting in the main as follows :—

To 100 parts castor oil, of good quality, are added in small portions at a time, 20 to 25 parts sulphuric acid of 65 to 66° Be′.

The operation is conducted in a stoneware, lead, or enamelled iron vessel, which is immersed in water in order to prevent the temperature from rising above 30 or 35° C., the mixing is effected by a wooden stick or spatula, or by mechanical agitators, and in adding the acid care is taken that it is poured in a thin stream, and that the whole quantity of acid is added within the space of 8 or 10 hours. The mixture is then left in contact during the night, and next morning is poured into a cask of either water or a solution of common salt, and well agitated ; after settling, the acid water which forms the lower layer is drawn off by the tap near the bottom of the cask, and the oily product which remains is mixed again with water, and after settling again separated from the water, and finally neutralised, either by means of a lye of carbonate of soda, or in some cases by ammonia.

The most important part in, preparing this oil mordant is to meet the exact point of neutralisation, which is readily done after a little practice, and by the use of litmus or turmeric paper.

If caustic soda is employed in the neutralisation, the fatty acid should not be completely neutralised with caustic soda, but only enough of the latter should be added to effect the neutralisation of, say four-fifths of, the product, and the remainder should then be neutralised with ammonia, since a little excess of the latter will not act as injuriously as an excess of caustic soda.

Ammonia imparts to the oleine solutions the property of dissolving a larger proportion of water, and thus weaker commercial products are obtained.

The oleines, or alizarin oils of commerce, are sold according to the amount of fatty acid they contain, as 50 or

75 per cent., and it is necessary to estimate the percentage of this acid.

A rough method consists in treating a sample with weak sulphuric acid solution until it shows a decided acid reaction, and, after well shaking, adding enough common salt to obtain a saturated solution in the quantity of water used. The test can be performed in a small flask, the neck of which has been graduated in cc., and the amount of fatty acid which separates from a given amount of the commercial product can at once be read off. A modification of this method consists in placing a few cc's of the sample to be tested in a graduated glass cylinder, and after adding enough weak sulphuric acid until it shows an acid reaction, to shake well, and place the cylinder in hot water, and after cooling to 15° C. read off the separate fatty acid.

A more exact method of estimation has been recommended by Stein, and is conducted as follows :—

10 grs. oleine or alizarin oil are mixed with 75 cc. saturated salt solution in a glass beaker, and the whole heated to the boiling point, when 25 grs. wax are added. After cooling, the wax cake, which contains the fatty acid, is washed with water, then slightly dried between layers of filter paper, and exposed for 12 hours in a covered glass jar over sulphuric acid. After weighing, the difference in the weight of the cake, 25 grs. will indicate the amount of fatty acid from which the percentage can be calculated. From the percentage thus found three per cent. must be deducted, because the fatty acid is being weighed as hydrate.

Castor oil is generally employed in the preparation of these commercial oleines, though olive oil can also be used for the purpose with almost the same results on the cotton goods, but as the latter is more expensive than castor oil, there is no advantage. The castor oil preparations, especially those prepared with a lower quality of oil, impart to the goods the peculiar smell which distinguishes the oil itself, but this has not proved a hindrance to its employment.

Other methods of preparation of the oil mordants have been recommended, for instance, the oil is first of all saponified by means of caustic soda, then the soap is decomposed with weak sulphuric or hydrochloric acid, and the fatty acid thus obtained is treated with ammonia. This method is more expensive, and does not offer corresponding advantages.

The treatment of oil with hypochlorites has also been tried, but so far does not seem to have been largely employed.

On the theory of the prepared oils by the sulphuric acid process, different opinions prevail among chemists. Messrs. Liechti and Suida have investigated the matter very fully, and, according to their report, when olive oil is treated with half its weight of sulphuric acid, and after standing for 24 hours, washed with salt water, as by the ordinary method, the product obtained consists of two substances, one soluble in water the other soluble in ether.

The product soluble in water is the oxyoleic-glycerin-sulphuric-ether, and forms soluble combination with alkalis, but insoluble compounds with alkaline earth and heavy metallic oxides.

The product insoluble in water, but soluble in ether, is the oxyoleic acid, $C_{18}H_{34}O_3$, which also gives insoluble compounds with alkaline earths and heavy metals. Other secondary reaction also takes place. Castor oil behaves in the same way, and the two corresponding products, one soluble in water, the other in ether, are also obtained.

In the treatment with sulphuric acid an oxidation takes place, according to Liechti and Suida, by the sulphuric acid, which is reduced to sulphurous acid. The reactions are therefore of rather complex character.

The theory of the behaviour of these compounds thus formed, in the process of turkey red and alizarin red dyeing, brought forward by the same authors, is not accepted by many chemists, among others by Müller-Jacobs, to whom is due the introduction of the sulphated oils into practice, although the method of preparing olive oil with sulphuric acid was originally recommended by the chemist Runge, many years ago.

SOLVENTS.

In the preparation of colours for printing, and also in the production of many mordants, some products are employed which react either as solvents by their own property or by preventing the combination of the mordant with the colouring matter, and the formation of a coloured lake, which only takes place when the solvent has been driven off, as, for instance, in the preparation or fixation of steam colours.

Acetic Acid ($C_2H_4O_2$) is the most useful organic acid employed in dyeing and printing, being utilised in many processes, either in the free state or in combination with metallic compounds as acetates.

The manufacture of acetic acid is a very important one. In the distillation of wood a raw acid is formed, which is collected and combined with lime, and the product is then brought into commerce as acetate of lime. From this, acetic acid is manufactured by distillation in connexion with hydrochloric acid. Acetic acid comes of different qualities in commerce, mostly in an impure form as *Wood* or *Pyrolignous* acid of about 6 to 10 or 12°Tw., often largely contaminated with organic substances, and of brown colour.

Commercial acetic acid contains lead, and sometimes, but seldom, other metals also, in solution ; in this case the acid cannot be well employed in the preparation of those colours or mordants for which a complete freedom of iron, lead or copper, is an absolute condition. Sometimes the commercial product contains free sulphuric acid, which is added in order to precipitate out any lead dissolved in the acid during the manufacturing process.

According to the purpose for which it is intended, a more or less pure product is required, and in addition to the quantitative analysis of the samples, it is necessary to test by practical trial, to see that the shades produced are not impaired by the organic or inorganic impurities of the acid. The degree of Twaddle is by no means a sure indication of the strength of acetic acid, especially for the impure qualities, and consequently a quantitative test by volumetric analysis is necessary. Commercial acetic acid of 9° Tw. contains about 30 per cent., while the one of 10° to 12° Tw. may contain 50 per cent. pure acetic acid, or more.

GLACIAL ACETIC ACID, chemically pure acid, crystallising at 17°C., is seldom employed in dyeing and printing, but to a certain extent is used in the manufacture of aniline blues.

TARTARIC ACID ($C_4O_6H_6$).—A well crystallised organic acid obtained from tartar or argals, and is soluble in 1½ parts of water.

It is employed in the preparation of several steam colours, and its great importance is in the discharging process of turkey reds in calico printing. It is also useful in resisting and discharging iron or alumina mordants.

The commercial product is tested for the amount of pure acid by alkalimetry, and at the same time it is ascertained if free from sulphuric acid. A pure product contains up to 99½ per cent. pure tartaric acid.

CITRIC ACID ($C_6H_8O_7 + H_2O$) comes in commerce either in the form of a crystallised product, or in solution, under the name of *Lime Juice*, being in this instance the juice of lemons, which has been pressed out and put into casks for export. Although containing, in addition to the acid, a pretty large amount of organic substances, very prone to fermentation, the commercial lime juice keeps much better than might be expected, owing to a small amount of etherical oil, which, by floating on the surface of the liquor prevents it coming in contact with air. The commercial lime juice is very often adulterated with tartaric acid, and sometimes also with sulphuric acid. The latter can be easily detected by testing a sample with a solution of chloride of barium.

In testing commercial samples, either of the crystallised product or of the solution, the amount of pure acid is estimated by titration; good crystals contain 99 per cent. citric acid. It can be ascertained if the crystals of citric acid are adulterated with those of tartaric acid by putting a small sample on a glass plate and pouring a little caustic potash over it. If tartaric acid is there the tartrate of potash will crystallise out, while the citrate is deliquescent.

Commercial lime juice shows generally alout 45° Tw., and may contain from 20 to 40 per cent. citric acid.

Citric acid is very largely employed in printing in the preparation of acid discharges on alumina or iron mordants, in the madder styles, and also for the purpose of resisting the same metallic oxides.

OXALIC ACID ($C_2O_4H_2 + 2H_2O$) is found in commerce in well crystallised form, generally of good quality and containing 99½ per cent. of pure acid. Its employment is not a very extensive one in printing, but it does good services as a solvent in the preparation of some steam colours, and is also useful in the preparation of mordants.

Oxalic acid reacts on cotton by steaming like a mineral acid, asserting a destructive action on the fibre, while tartaric and citric acids are innocuous under the same conditions.

GLYCERINE ($C_3H_5(OH)_3$) is obtained as by-product in the manufacture of stearine candles, and also in the manufacture of soap. The purest glycerine, as used for dynamite making, shows 30° Be′. The lower qualities are of a brown shade, while the purer are quite colourless. Glycerine is very often adulterated with glucose syrup, and its analysis is a rather delicate operation, as the majority of methods recommended for the testing of glycerine are unreliable.

Glycerine is employed in the preparation of arsenious acid mordant, and also as solvent for some aniline colours. For finishing purposes it is also found very useful, as it gives softness to the finish, and it keeps the cloth soft, while it attracts a little moisture from the atmosphere at the same time. The qualities generally employed in dyeing and printing show, as a rule, 28° Bé or less.

ACETINE.—This preparation has been quite recently recommended for use in preparing steam coal tar colours for printing. It is obtained by heating to the boil for 48 hours, in an apparatus with inverted condenser, glycerine with double its weight of glacial acetic acid, when etherisation takes place, and a mixture of mono and di-acetine is obtained, which forms an excellent solvent for these coal tar dyestuffs, which are fixed by means of tannic acid, even those insoluble in water, such as the indulines, &c. The chlorhydrines behave in the same way.

BISULPHITE OF SODA $\substack{Na\\H}SO_3$, has become a very important product in the hands of the calico printer, dyer, and colour manufacturer. It is useful as a reducing agent, as in preparing the indigo vat with the hydrosulphite process, and acts also as a solvent, and enters in the preparation of several colours for calico printing. It is produced on a very large scale by the action of sulphurous acid gas on soda crystals. The *hydrosulphite* is called by many English chemists *hyposulphite,* although by the latter is generally understood to be the $Na_2S_2O_3$, the hyposulphite or thiosulphite of the photographers. The hydrosulphite is the derivative from hydrosulphurous acid of Schützemberger. H_2SO_2.

THICKENING OR SIZING MATERIALS

EMPLOYED IN THE PRINTING AND FINISHING OF CALICOES.

In the following chapter I purpose to give in a succinct form the principal characteristics of the materials generally employed for thickening or sizing, and to indicate at the same time the quickest and simplest methods for testing or estimating their commercial value. Under the name of thickenings are understood such preparations as are generally added along with the colours in order to give them the necessary amount of consistency to allow them to be printed on the required spots to produce the patterns without being liable to run. In other words the part played by the thickening is simply a mechanical one, while if the colours are required to be permanently produced on the fabrics, mordants or other fixing agents are necessary for the proper chemical fixation of the different shades. The thickening substances are generally some varieties of the gums or amylaceous matters so plentifully found in the vegetable kingdom, such as starch and its derivative dextrin, etc., and the gums of different kinds, such as gum arabic, senegal, tragacanth, etc. They belong to the class of carbohydrates, having the same empirical formula as cellulose, to which they show great analogy in their properties and reactions.

THE STARCHY SUBSTANCES.

These are generally employed as thickeners, or as sizing or finishing materials; they are mostly composed of amylum or starch, being in fact in many cases this substance in its pure form.

AMYLUM OR STARCH ($C_6H_{10}O_5$), is found very largely spread in nature, being the principal constituent of some seeds, as for instance in the case of cereals ; it is also found in the roots, stems, and fruits of many plants. Starch is found in the form of minute granules which, although possessing the same chemical composition, still show a great variety in their characteristics, according to the plants from which they are derived, especially on account of their sizes and shapes when viewed under the microscope, and it is through this fact that by the microscope the different starches can be distinguished from each other. Starch is a white substance insoluble in cold water, but possessing the peculiarity, when treated with boiling water, of swelling and forming a kind of gelatinous mass, the so-called starch paste, a property for which it is utilised in practice, since by this process of boiling, the starch granules largely increase in size, and absorb at the same time a large quantity of water, and if the amount of water and starch have been taken in the right proportion, all the water is taken up and a jelly-like mass is formed, from which the water cannot be separated by mechanical means. not even by straining it through cloth. To this valuable property of starch granules is due the employment of starch in calico printing, since by being capable of absorbing solutions of mordants and colours, and keeping pigments in suspension, it enables printers to obtain mixtures capable of being properly printed on cotton. A very characteristic reaction of starch is, that when boiled with water, it gives a blue colour when treated with a solution of iodine in iodide of potassium. The different varieties of amylaceous substances employed are the following:—

WHEAT STARCH.—This is a very important product for calico printers, and is the thickening material mostly employed in the preparation of colours to be printed on the roller printing machine. As it is more expensive than some of the other varieties, it is sometimes adulterated with potato starch, etc. In testing wheat starch, first estimate the amount of water by weighing a small sample in a porcelain capsule or watch glass, and drying in a drying closet or stove until the weight obtained is constant, the difference in weight from the first and last weighing will indicate the amount of moisture, which in good air-dried starch ought not to exceed 14 to 15 per cent. It is also well to estimate the amount of ash by incinerating a small sample, since in some cases starches are adulterated or weighted by means of white mineral pigments. Pure starch contains a very small amount of ash, about .2 to .4 per cent. The admixture of wheat starch with potato or other cheaper starches can only be detected under the microscope. This can easily be accomplished by procuring tables showing the form, etc., of the different varieties of starch granules when viewed under the microscope, and comparing with the samples under examination. The most handy and at the same time also very reliable test is by boiling with water to form the starch paste; the test of the different brands being done by comparison with a sample of known quality, which should be kept in a well stoppered glass jar. The method is as follows:—

In an enamelled iron beaker or saucepan, or in a copper vessel, capable of holding about 300 to 350 cubic centimeters, add

200 cc. cold water.

then

20 grms. of the starch sample.

Stir well with a wooden spatula until all the lumps have disappeared, then place the vessel on a Bunsen burner or on a good charcoal fire, and stirring the contents with the spatula all the time, boil for a few minutes. It is advisable to have the boiling vessels provided with a handle by means of which they can be held in their place with the left hand, while in the right the wooden spatula is kept for stirring, especially when boiling, and taking care to agitate well by touching the bottom of the vessel with the spatula to prevent the starch from burning. After boiling, the vessel is removed from the gas or fire, and the stirring continued until the paste is cold; the cooling can be hastened by placing the vessel in cold water. It is well in conducting these tests to do them at the same time, or at all events one after the other, but if many tests have to be made at once then it is well to have an oil bath at hand heated by gas or free fire, having a perforated cover through which the vessels are allowed to stand in the oil; in this way they are exposed to the same temperature. At the same time care must be taken that all the samples are being stirred, if not continuously at all events repeatedly. Laboratories having small copper boiling pans on the model of those used in the printworks, with double bottoms heated by steam, are even better situated for testing starches, since they are placed in the same conditions used on the large scale.

When the starch paste is cold, especially if a comparative test has been made, the quality of the starch can be judged by the consistency or thickness of the paste. The test must then be extended further, and made more practical by trying the thickening in printing. If two or three samples of starches are tested at the same time the colours prepared for each can be tested side by side on the same roller. Another test of the starch paste is to leave the samples alone in open beakers or glasses and note the time they take to become sour; the longer the paste keeps the better is the starch.

Rice Starch.—This is seldom used for thickening, but is especially useful for the finishing or starching of goods which are strongly weighted. It can be easily distinguished from other starches when exposed under a good microscope with high magnifying power. In this case also it is well to estimate the amount of moisture and of ash, and at the same time, a practical finishing experiment will be necessary in order to give an idea about its usefulness for finishing purposes.

Potato Starch or Farina.—This is not much used for thickening, but is mostly employed for finishing. It is found in commerce containing various amounts of water, in some cases as much as 20 per cent. In testing this starch, after the moisture, the amount of ash must be estimated. Its thickening power, which is greater than that of any other starch, must also be tested by experimental boiling

10 to 15 grms. potato starch.

with

200 cc. water.

The longer the paste keeps before it turns sour, the better is the quality of the starch. It is distinguished from the other varieties also through the microscope.

Maize or Indian Starch is mostly used for finishing, but recently also in special cases for thickening, when very thick colours are required. It has been used with advantage in the new indigo printing process by means of glucose. The testing is effected by examining its thickening power by boiling with water, as mentioned before, and the amount of moisture and ash must be also estimated. In this case, too, a microscopical examination is necessary in order to distinguish it from the other varieties of starch.

Wheat Flour.—Though this article is sometimes used by calico printers for thickening purposes it is principally employed in the sizing of yarns before weaving. Starch is the chief constituent, averaging about 65 per cent. of the weight, but it contains also over 10 per cent. of gluten, a nitrogenous matter, and a small amount of sugar and dextrin, and is more liable to ferment than the pure starch. A good flour should be of a good white and devoid of smell, and of course free from acidity. In testing samples, the amount of moisture should be estimated, which ought not to be more than 16 to 18 per cent.; the amount of ash should also not exceed ·3 to ·5 per cent.; this latter test is especially of importance, since flour has been found in commerce very largely adulterated with plaster of Paris or even with carbonate of lime. A microscopical examination will be found useful, as also the estimation of the thickening power, by boiling in the usual way with water.

DEXTRIN.—Under this name are understood several products which are known in commerce under different names, such as *gum artificial, light and dark British gum, dextrine, calcined starch*, etc., they all being starch derivatives, being obtained from starch which is made soluble in water by several processes giving products which, although possessing different properties from starch, still show the same chemical combination ($C_6H_{10}O_5$.) Dextrin is produced by exposing starch to dry heat at 200° C., when, however, the product is pretty highly coloured. This is sometimes an objection in calico printing for light and bright shades. A method more generally adopted, and originally proposed by Payen, consists in treating 400 parts starch with one part nitric acid and enough water to form a stiff paste, to dry and then expose the mass to a temperature of 200° C., the product thus obtained being nearly colourless.

According to the quality of the starchy substance used in this process, for which generally the cheaper varieties, such as farina or maize starch are mostly used, a product of different quality and price is obtained. For instance, while some varieties are soluble even in cold water, some others only dissolve in boiling water. In testing commercial samples the following points must be borne in mind :—

First of all the purpose for which it is required, in which the colour of the product may or may not be an objection.

The amount of moisture ought to be estimated; this ought not to be generally more than 10 per cent., although it may be in some cases as much as 15 per cent. and as low as 5. The amount of ash can also be estimated and, of course, the solubility in water. The thickening power must be tested by practical trial by comparison with a standard sample, having, of course, regard to colour, quality of product and price. As a rule from 100 to 500grms. dextrin, or even more, are dissolved per litre of water, and this gum water is then used for practical printing trial.

As dextrin is sometimes used as an adulterant, not only for colouring matters but tannic acid, etc., its presence can be ascertained and even estimated by treatment with alcohol, which, in the case of tannic acid, will dissolve the latter and leave the dextrin undissolved. In order to ascertain the sort of starch from which the dextrin has been produced, the microscope may be well employed, as, although a change in the solubility has taken place, the structure of the starch granules can still be seen. Dextrin is generally employed in colours which it is intended should remain on the surface rather than penetrate into the fibre, and in the preparation of aniline black colours it is found especially useful, as the colours do not act so strongly on the fibre when dextrin is there as when starch alone has been used. The thickening power of dextrin is much less than that of the starch from which it has been produced—for instance, 1lb. neat starch is equal in thickening power to at least 5lb. of the calcined product.

GUMS.—The natural gums are products obtained as exudations from shrubs or trees, principally from some varieties of *acacia*, and are found in commerce under different names, the most important varieties being GUM ARABIC, GUM SENEGAL, etc. The commercial products vary considerably in price and quality, and to properly discriminate them requires a good deal of practical experience. A good gum should be easily soluble in water, and not leave too large an amount of sediment or undissolved product, in the shape of sand, wooden bits, leaves, etc. The solution must not be too deeply coloured, in fact, for light and bright shades the gum solution is required to be almost colourless. These gums are used only for fine work on account of their high price, and it is important that they should be of good quality. The testing of them can only be done by a practical trial by printing, the following points being however of importance :—Solubility, colour of solution, and amount of undissolved matter, &c.

Dissolve 100 grms. of the sample to be tested in 500 cc. (½ litre) hot water by agitating occasionally with a wooden spatula while heating gently for several hours on the water bath, and then leave to stand one night, and next morning filter the solution through a calico filter. Judge of the colour of the filtered solution by comparison with the standard sample, and at the same time compare them also for specific gravity by means of the Twaddle areometer. This, although not a very reliable instrument in this case, may be of utility if only by affording a comparison.. The insoluble residue on the filter after washing with hot water should be collected, dried, and weighed. But a proper test by printing should also be made by preparing a strong gum solution and using it in the preparation of the colours in comparison with a standard gum sample of known quality.

The cheap qualities of gum contain very often varieties which are not soluble in water, but which only swell up and form a kind of paste; these varieties will be at once shown by the filtration in the testing mentioned above. However, for some purposes these cheaper kinds can be very well employed, since the variety which does not dissolve in water is still useful as a thickener, but such gums should not be used when patterns with fine outlines are required, or when bright and clear shades are wanted. Gum solutions are largely employed in block printing with all colours, while on the machine they are principally used for light shades of steam colours, cutch browns, etc.

For estimating the thickening power of gums the so-called viscosimeters have been often recommended, but seldom, if ever, found of great practical utility.

TRAGACANTH, also sometimes called gum dragon, is more employed on the Continent than in England. It is derived from the shrub, *astralagus*, growing in Asia, and is brought into commerce in the form of thin strips, resembling sometimes leaves, sometimes mussel shells, of a whitish yellow colour. It is the most powerful thickener used by the calico printer: in fact, it has four times as much thickening power as starch; it is generally used when deep shades are required, but it is not very suitable for sharp outlines; it renders good service for styles which do not require much washing, when, if left on the fibre, it imparts to it a certain amount of stiffness.

For testing, soak 10 to 15 grms. tragacanth in 1 litre water for 24 hours, boil for several hours until the solution is complete, then estimate the thickening power by a practical trial.

Bad qualities of this gum soon become sour when made into thickening and left to stand for some time; it is a curious fact that acid starch thickening keeps longer with tragacanth than if employed alone; it is also advisable, when preparing colours with tannic acid and starch thickening, always to employ a certain amount of tragacanth. Gum water and tragacanth mucilage can very well be mixed with each other or with starch paste.

In the employment of all these thickening materials it is desirable to avoid as much as possible the presence of grit, which is the cause of much trouble and scratching of the rollers of the printing machines, not to mention holes in the pieces.

Of other thickening or finishing materials, linseed, mucilage, karragheen moss and algin, have been recommended and employed for special purposes, but only to a very limited extent.

THE ALBUMENOID MATTERS

May be considered both as mordants and mechanical fixing agents; in the first capacity they are now seldom employed for the fixation of aniline colours in printing, and scarcely ever for mordanting cotton, which is afterwards to be dyed with basic coal tar dyestuffs.

The great employment of albumens is for the fixation of pigments in calico printing, in which process they act mechanically by their property of being converted from a soluble into an insoluble product by coagulation, the colouring matter being thus permanently fixed on the fibre by the coagulated material in which it is kept imprisoned.

EGG ALBUMEN is the white of eggs, which is prepared for commerce principally out of hens' eggs. The manufacture of egg albumen is still an important one, and is conducted in countries and districts where poultry are abundant and eggs plentiful and cheap. After being separated from the yolk, the whites are collected and dried at as low a temperature as possible, by an apparatus on which the product is exposed to the action of heat and movement on a very large surface, as for instance, on large revolving cylinders, heated by means of hot water, or better still, hot air; or by placing the white of eggs in shallow porcelain or glazed earthenware trays, or even zinc vessels, in moderately heated stoves, sometimes also by the aid of vacuum.

The egg albumen of commerce forms transparent yellowish, amberlike pieces, of small size, sometimes resembling colophony. It can be easily converted into powder, but if it is in small pieces it is better to dissolve it as it is, or only after a slight grinding; it should dissolve thoroughly in water, or leave very little undissolved. In preparing solutions of albumen, cold or lukewarm water is employed, but the latter must not be more than 30 to 35°C, since albumen solution begins to become misty at 60°C, and coagulates at about 72° to 75°C.

The coagulation of albumen is also effected by mineral acids, principally by nitric acid, and in a less degree by hydrochloric and sulphuric acids, which coagulate albumen solutions at ordinary temperature, and to this property is due one of the applications of albumen, the producing of discharged coloured patterns on indigo dyed goods. Albumen is also coagulated by some metallic salts, and alkalis rather retard the point of coagulation.

Albumen is a nitrogenous matter, and contains also sulphur. It belongs to the class of organic products known as proteine substances. Albumen solutions are very apt to go into decomposition with development of sulphide of ammonium, and for this reason they must not be kept too long before they are used. In order to prevent decomposition a small amount of arsenite of soda or chloral hydrate is very often added; a solution in glycerine stands also better than one in water. When exposing albumen colours to the steaming to coagulate the albumen, a certain amount of sulphuretted hydrogen is formed; this is the reason why lead colours blacken during the steaming process.

Commercial egg albumens are often adulterated with gum or dextrine, and these adulterations are rather difficult to detect. The commercial value of samples is best tested by printing in comparison with a standard sample, the albumen solutions being prepared by dissolving one part albumen in two parts water; any pigment can be employed for the trial, but preferably ultramarine, and those producing light shades. In dissolving the albumen samples they must be left standing for about 24 hours, stirring occasionally, in order to bring as much of the albumen as possible in solution. Any insoluble portion can be easily estimated by using a larger quantity of water in making the solution and then filtering and washing, drying and weighing the insoluble product left on the filter. The amount of coagulable product can also be estimated by dissolving 5 to 10 grammes of the sample in water, filtering through paper, and allowing the filtrate to fall into a vessel containing a boiling alum solution. The coagulated product is placed on a filter, and, after washing and drying, is weighed, the amount in samples of good quality ought to be about 95 per cent.; if the variation is more than 5 per cent. the sample is adulterated.

The great value of the egg albumen is not so much owing to its power of coagulation, but to its light colour, which does not spoil the delicate shades of the colours when printed on calico, and for this reason a higher price is paid for it, consequently this must be taken into account in discriminating between the different brands of commercial articles.

Printing colours prepared with albumen have a great tendency to froth, which is a great objection, as some of the printed shades do not come out clear and distinct; it has been found necessary therefore to add a certain amount of turpentine to the printing colour, which to a very great extent removes the drawback.

Blood Albumen.—This product is the dried serum of the blood of slaughtered animals, after separating from the fibrine, and is brought in commerce in large quantities. The manufacture of this article has been considerably improved in the last few years, with the object of obtaining as nearly as possible a colourless product which could be substituted for the more expensive egg albumen.

So far, however, although blood albumen can be found in commerce of good quality, the product of the egg is still used in preference when delicate shades are required. In discriminating among commercial samples the great point of importance is the colour, or rather the absence of colour, the lighter the better; the amount of insoluble and of coagulable product can also be estimated, but a printing trial with a standard sample will be the most reliable test, as it gives at once an idea of the coagulating power in fastening the pigments on the fabric, and also indicates its adaptability for the production of fine, bright colours.

Many attempts have been made to bleach blood albumen, and thus make it equal to the egg albumen, but so far without success, although the qualities have been considerably improved in the last few years, and are employed with success for ordinary work.

Blood albumen coagulates at about the same temperature as the egg albumen, viz., 72 to 75°C, and behaves almost in the same way in the fixation of pigments. It possesses the same chemical elementary composition, but it is not identical with the other; in fact the chemistry of the albumenoid products is not as complete as it might be, and we are much in the dark yet about the constitution of albumen, some chemists even asserting that not only the albumen is different in the eggs of the different birds, but that the white of the hen's egg is itself a complex product, and not one body only, as generally accepted. The theory of coagulation of the albumens is also not quite satisfactorily explained, since it is admitted that the product is converted into an allotropic modification without any change of composition.

CASEINE OR LACTARINE

Is not largely employed in calico printing for the fixation of pigments, in the same way as albumen, as it does not yield such fast colours. It possesses the same elementary composition as albumen, but is far from possessing the same fixing properties. The commercial article, which is in the form of a yellowish white powder, is obtained from skimmed milk by precipitation with weak acids, then filtering, washing until free from acid, and drying.

Before use it is dissolved in diluted ammonia or borax solution, but its employment is limited except for special purposes, especially when light shades are required.

Its action is not quite similar to that of albumen in the fixation of the pigments on the fabric, and can scarcely be called a coagulation, neither do the colours stand soaping so well. A practical printing trial can be made in comparison with a standard sample, and a chemical examination as to its solubility, &c., should also be made.

Some preparations of caseine have been recommended for use in printing, such as the caseine magnesia, or the product obtained by heating caseine with nitric acid, in both cases it being stated that a better fixation is effected than by means of the ordinary product.

GLUE AND GELATINE

Find pretty extensive employment in dyeing, not so much as mordants, or for the fixation of colours, but for the keeping of the whites clear when dyeing pieces in the alizarin dye beck.

It has not been thoroughly explained in which way glue acts in preventing the whites from being soiled during the dyeing process, but it may be admitted that glue, in connection with the tannic acid, forms an insoluble compound which is mostly fixed on the white, and acts thus as a kind of reserve; and it is a well known fact among practical men that an addition of glue to the dye beck helps considerably in obtaining a better white than if no glue is used.

Glue is also a nitrogenous substance of the protein group, and is very liable to decomposition.

It finds extensive employment in finishing goods when a stiff finish is required. In testing commercial samples a practical trial can be resorted to ; but the colour of the samples their solubility in water, smell, &c., may serve as guides, or a chemical examination may be made by precipitating the glue out of a solution by means of a standard tannic acid sample, but in this case the test can only be a comparative one with standard sample of glue of known quality.

WATER.

The question of the quality of the water is of the utmost importance for a bleach and printworks. The first condition should be a constant and plentiful supply, and the other, and not less important one, that the quality should be good. A great deal of experience is required in the descrimination of the proper water supply, and it requires a close acquaintance with the practical industry of the branches for which the water is required, since the chemical examination alone will not give any indication as to water being good or otherwise for a given purpose.

For a bleach works the softest water is the best, while for some branches of dyeing and printing a moderate degree of hardness is not only not injurious but even beneficial, as for instance in the case of turkey reds. In the majority of cases the presence of iron is objectionable, and a water containing this impurity is thoroughly unfit for employment in alizarin red dyeing and printing, and also when employing coal tar colours, which are fixed by means of tannic acid.

The majority of large works are supplied with reservoirs, in which the water is kept both for the purpose of storage and for the mechanical purification by resting, when the particles in suspension fall to the bottom and the water becomes clear. In many cases, however, a more rapid process is required, and this is effected by filtration through beds of stones, gravel and sand, arranged in layers, beginning with large river stones at the bottom and following with layers of smaller size, up to those of gravel, and the whole covered by a layer of clear river sand. The water is introduced from a pipe at the bottom, and ascends slowly through the different layers, thus becoming clear, and comes out by a pipe or spout at the top of the tank or reservoir. According to the quantity to be filtered, the size of these filters vary. The larger sizes are constructed of bricks or masonry, while wooden vessels can be employed for filtering smaller quantities. These simple filtering arrangements do good service, and are not expensive. After being used for some time they can be cleaned by reversing their action, by sending water from the top to the bottom and running off the muddy water at the bottom, the overflowing with water being continued until the water comes out perfectly clear.

There are several other arrangements for the rapid filtration of water, relying on different mechanical principles, which need not be discussed here.

The chemical purification of water to remove either the temporary or permanent hardness has attracted considerable attention, and many proposals have been made, the most useful method relying on the employment of lime water or milk of lime, as by Clark's process, or lime and caustic soda, which latter removes the permanent hardness at the same time, and several useful mechanical arrangements have been devised for carrying out these processes on a large scale, which have been fully illustrated and described in recent English publications and technical and scientific journals, to which I refer those interested in this matter.

The question of a proper water supply is, I repeat, a very important one to the bleacher and calico printer, as it forms the basis of success or failure of the industry, and it is a much more difficult subject to contend with than many people think.

THE PURIFICATION OF WASTE WATERS of bleach, dye, and printworks is also a matter of importance, especially on the Continent, where works are under strict supervision to prevent the pollution of rivers. Here managers and chemists find even a difficult question to deal with, and one on which very little can be said in a general way, as everything depends upon local circumstances, and upon the style of work carried on in the respective establishments; the general principal acted upon is precipitation of the impurities by different methods, and elimination of the precipitates by settling, or more rapidly by filtration.

The question of water generally can only be handled by chemists possessing, besides a good theoretical knowledge of the matter, extensive experience of the branches of industries for which the water is required.

PRINTING PROCESSES.

The methods of fixation of the different colouring matters in printing vary considerably, according to the nature of the dyestuffs, but they can be divided into two distinct classes, comprising the production of

1st—Printed (direct) colours.
2nd—Dyed colours.

The dyed colours are produced either by first printing the mordants, then fixing and dyeing in a bath with the colouring matters, or the cloth is dyed all over and designs produced by the resisting or discharging processes which will be mentioned later on.

The printed or direct colours are applied at once on the cloth and fixed by different methods, relying either on the steaming, oxidation or reduction process, &c., and are therefore styled steam or oxidation colours, &c.

The methods of fixation of the different dyestuffs will be first described individually, and then a short description of the grouping of the different methods, which are generally known under the name of styles, will be given.

In well regulated works, before the dyestuffs or drugs are applied on the large scale, they are tested in the laboratory, in order to be certain that they give the desired result, and as the training of those who are called afterwards to fill the positions of managers, chemists, or owners of printworks, must be begun in the laboratory, I have thought it advisable to describe here the methods of fixation and testing of the colouring matter at the same time, and consequently the proportions are given both in the metrical and English systems, in other words, both for the convenience of laboratory chemists and practical men.

The direct method of fixation, especially of the steam

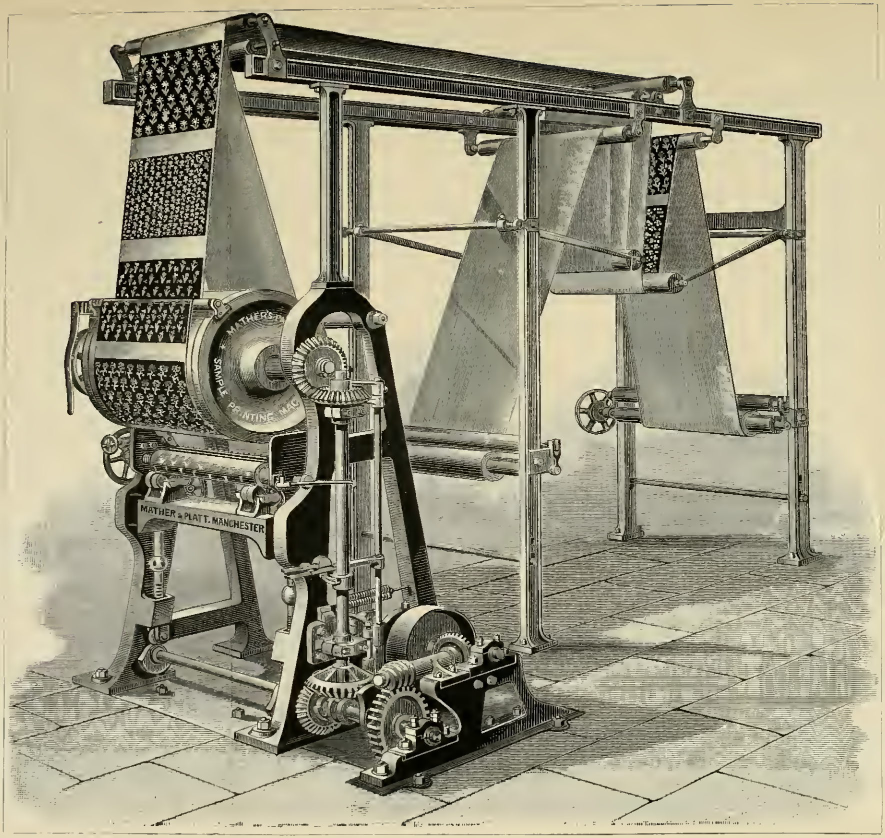


PLATE V.—SAMPLE PRINTING MACHINE.

colours, forming now the most important class, they will be first described.

The manipulations in printing being of a more complicated character than the operations of dyeing, the testings by printing are necessarily of a more complicated nature, and of course different appliances are required. The first absolute condition is to have a printing machine at command, and if the testings are done in print-works an ordinary one-colour printing machine will do, or the sample printing machine, as shown in the illustration (Plate V.), can be used; but if the tests are to be done in the laboratory, it is necessary to have a small roller printing machine, for without this no proper estimations can be performed. The most useful patterns for the purpose are stripes of about ¼in. to at most ⅜in. or ½in. on a white ground. The small roller of the printing machine ought to be at least 9in. in length, and as thin and slight as possible, so that it can be easily removed from the machine. This is an advantage easily appreciable by those who have much work to do, and who know how annoying it is to have to remove a cumbrous roller from a small printing machine in order to clean it when it is being constantly used. The doctor ought to be properly sharpened and level. As a rule this doctor is used at the same time as a colour box, and bits of calico are placed on each extremity of the doctor and pressed on the roller, so as to prevent the colour from running off. It is of advantage to be able to test two or three colours at the same time, and this can be easily done even on a small roller of about 9in. to 10in. in length. Suppose the roller has been engraved with nine stripes, then, besides the two bits of calico which are placed on both ends of the rollers, another piece is put in the middle and pressed pretty tightly between the roller and the doctor, so as to prevent the colours on both sides from running into each other. If three colours are to be tested at the same time, then, two bits of calico are used instead of one, so as to form, so to speak, three different colour boxes, each supplying three stripes. When no printing machine is at hand a block will have to be used for the purpose, but this method, except in skilful hands, does not give reliable results. The most convenient pattern to have on a block is formed also by stripes, which, however, cannot be very wide, 3-16ths of an inch being more than sufficient. While on the rollers of the printing machines the stripes are engraved, or, so to say, cut into the copper, and this cavity contains the colour, on the block; it is the pattern which stands in relief, and the space which has to remain white is simply cut into the wood. With a little practice pretty good testings can be performed, even with a wooden block, as it is not so much a question of obtaining a very fine print as to obtain shades of prints comparable with each other, as it is needless to say the tests are simply comparative. For block printing the following plan can be recommended.

First of all gum arabic solution is to be employed as a thickening, as it is more easy to obtain good prints by this than by means of any other thickening. The colour must be prepared neither too thin nor too thick, and must be spread as evenly as possible by means of a brush or by a glass or wooden stirrer on a piece of thick felt or printers' blanket, or any suitable material either stretched on a frame or simply nailed at the sides by means of tacks, and stretched on an ordinary table. The block is applied on the colour previously spread on the felt, so that it takes it as evenly as possible, and then printed on bleached calico, which is spread carefully over several layers of calico or blotting paper, or better still on a piece of printers' blanket covered with calico. By working with care, after a little practice, fairly good impressions can be obtained by this means. Two colours could be printed side by side by having a pretty long block, which is made to take at the same time two colours which have been spread side by side, without of course running into each other, on a piece, or better on two separate pieces, of thick felt or printers' blanket, and printing without any further trouble. As said before, with due care good results can be obtained by testing colouring matters by printing with the block, but of course more reliable results are obtained by the use of the printing machine. Still it must not be forgotten that block printing is still used in printworks to a larger extent than is generally believed, and in those establishments where block printing is in practice there is no other choice than to test colours by the block if by this means they are printed on the large scale. In order to transfer the colour properly to the blocks instead of the arrangement mentioned above, the following plan is preferred: a piece of woollen cloth or felt is stretched on a frame and nailed on the sides, and the whole is made to float in a box which has been filled with old colours or thickenings; by applying the block on the colour, which is spread on the surface of the woollen cloth, the latter, not resting on a stiff surface, easily yields to the pressure and gives up the colour more evenly. In some cases india-rubber bags are used filled with water. As many colours are printed and fixed by steaming it is well to have at disposal a small steam chest made of wood, with thick and strong sides. The chest is provided with a door for the introduction of the patterns, which are wrapped up in flannel and left to lie on a board or sticks supplied at the upper end of the chest. Steam is introduced through a pipe on one side of the box, a few inches from the bottom, and between this and the perforated double bottom. A tap is supplied at the bottom of the box to take the condensed water away. Or better still a closed steam chest made of cast or plate iron is put up which can be worked under pressure; 4lb. to 5lb. pressure to the square inch is quite sufficient for ordinary work, but for some cases, especially for alizarin prints, a higher pressure is employed to give a greater brightness to the shades. Where no steam is to be had the work has to be performed either with an ordinary kitchen kettle or any other copper or iron vessel supplied with a lid, the pattern being placed, wrapped in flannel, between the vessel and the lid, and held down by means of weights; it is, however, a cumbrous and makeshift arrangement, which gives a lot of trouble, the colours being very often spoiled by the water which condenses on the cloth. However, it is very easy either to buy or to have constructed a small boiler either of copper or iron, which can be heated by gas, and which is supplied with the ordinary fittings—steam-pressure gauge, safety valve, glass tube for the water level, etc., and to connect the same with a small steam chest, or even with an iron or copper pipe, which is perforated and made to stand upright, and round which a piece of flannel is wrapped, and then the prints to be steamed are wrapped between two layers of flannel, the whole being enclosed by a thick woollen cover and a zinc sheet, which is bound all round by strings, so that the whole forms a kind of flannel cylinder round the perforated iron or copper pipe.

This arrangement works well, and is preferable for these experiments, in which the prints are to be exposed to very hot steam, the pressure in the boiler being regulated according to requirement. If such a miniature boiler can be procured, or steam is at hand, then it is advisable to arrange a wooden box, which could be used also as a continuous steamer or an ageing machine.

Of the other apparatus necessary for conducting printing experiments and testing of dyestuffs the following must also be mentioned:—If steam is available, double-cased copper boiling pans, heated by steam, ought to be procured. These may also be produced, of a similar size, exactly on the model of those used in the colour shops of printworks for preparing the thickenings, and they are very useful, but unfortunately very expensive. If these colour pans cannot be had we have to be satisfied with simpler arrangements. In this case ordinary tinned, or, better, enamelled saucepans should be resorted to. They can be firmly held by the handle while the contents are being stirred by a wooden stirrer, as in the case when boiling starch to prepare starch paste thickening. The saucepans are heated on a gas lamp, or on a charcoal or coke fire if gas is not available. It is needless to say a good pair of scales, with pans, are of absolute necessity for weighing the dishes or

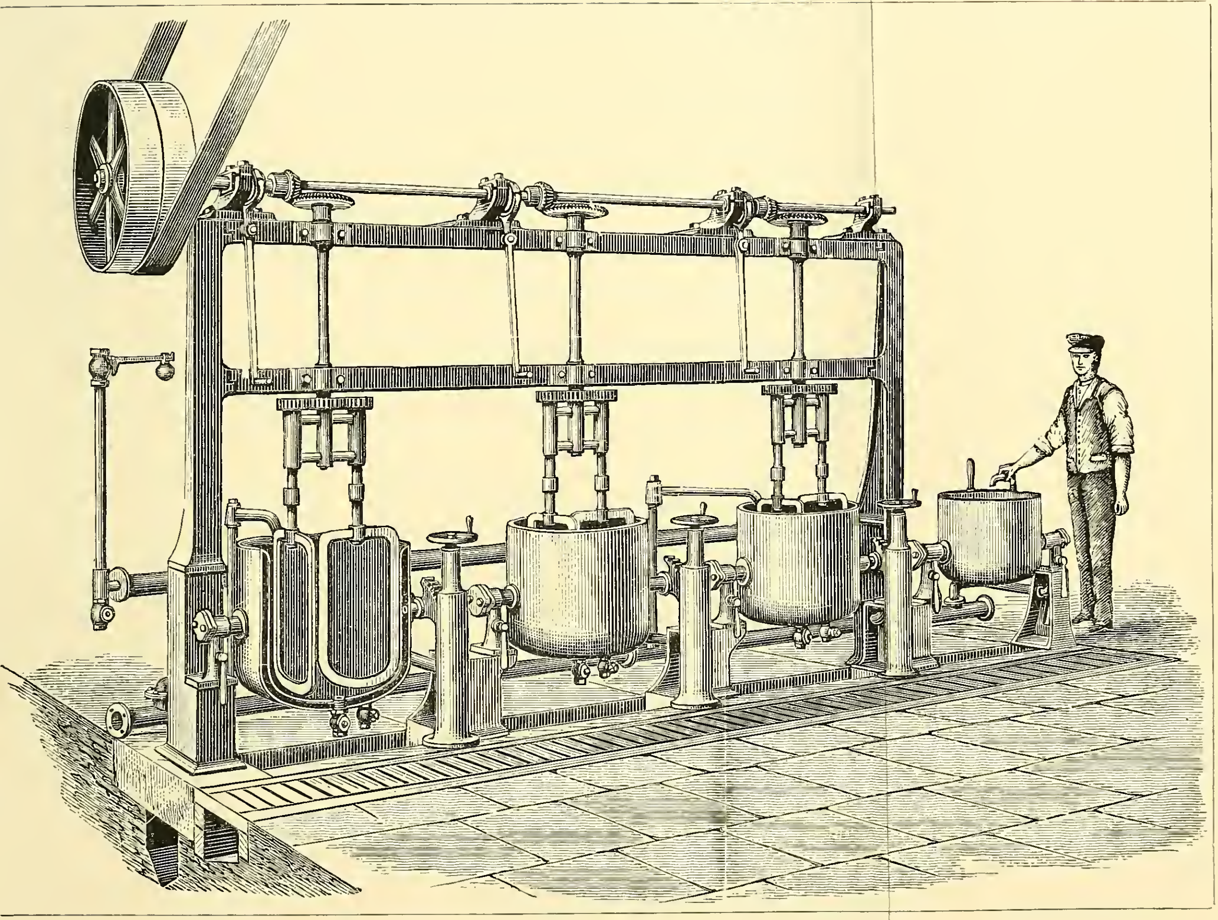


PLATE VI.—COLOUR PANS

the capsules in which the colours are being mixed. It is also necessary to have a small pair of hand scales, besides large and small sets of weights, and of course graduated measures, pipettes, porcelain dishes or capsules, and large and small enamelled iron dishes, wooden spatulas, glass rods, etc. It is also advisable to have standing glasses on the model of those used by apothecaries, which are graduated in simple proportions, say in ½oz. or 1 oz. If these cannot be had it is an easy matter to graduate ordinary standing glasses, or even small beakers, in simple proportions, for instance by marking them at every 25, 50, or 100 cubic centimeters, by scratching the glass on the outside by means of a file. This it is advisable to do because in many cases the colours are mixed by taking the ingredients in simple proportion by measure, the measuring being more expeditious than the weighing.

For mixing colours, except in special cases, small wooden spatulas are preferable to glass rods, and everyone can easily make them by using a penknife.

It is also advisable to keep standard solutions or preparations of the products which are constantly being used, to save the trouble of preparing them over and over again. For instance, it is advisable to prepare a standard arabic gum solution beforehand, and keep it in well closed vessels for use, the quantity prepared being in proportion to the amount of work which is being done. Mordants or other preparations for fixing colours, etc., ought to be prepared beforehand and kept in well stoppered bottles, duly labelled for use. Of course these remarks refer only to those preparations which will stand keeping, but starch paste, albumen liquor, etc., had better be prepared either fresh every time, or at all events at short intervals. A convenient quantity to prepare of each standard preparation is one litre (1,000cc).

As in some cases the mordants are first printed on calico, and the colours fixed by dyeing, it is in this case necessary to have apparatus at hand to perform dyeing operations on a small scale. For this purpose the same appliances can be recommended as employed in the testing of dyestuffs by dyeing; that is, either porcelain capsules or enamelled iron dishes heated on a gas flame can be used, or if several dyeings are to be performed at the same time it is advisable to have either copper, glass, or earthenware vessels, heated on a water or an oil bath, according to the temperature required. A very practical arrangement is to have these heating baths made of iron or copper, with a perforated lid, through which the vessels are immersed either in the oil or in the water. Preferably earthenware vessels are used of a capacity of a little over one litre, possessing a rim on the outside, about one inch from the top, which allows the vessel to sit on the lid of the heating bath, being at the same time immersed in the heating medium without touching the bottom. These water baths can be heated by steam or gas, while the oil baths are heated by gas or on free fire.

Of the colours which can be fixed by steaming we have in the first instance the pigments, then the aniline or coal tar colours, and the dyewood extracts, among which must be mentioned indigo, and some mineral colours. The pigments fixed by means of albumen, the principle of their fixation relying on the fact that albumen becomes coagulated by the action of the steam, and thus keeps the pigments imprisoned in the coagulated substance, and permanently fixed on the fibre, so that they cannot be removed either by washing or soaping. Although the pigment colours are not so much used now as they were formerly, they are still employed to a certain extent. At the beginning of their introduction the aniline colours were also fixed by means of albumen, and this method is even now used by some printers, and supplies a simple means of testing some of the aniline colours.

Before describing the different processes for fixing the colours by printing, it will be of advantage to describe first the preparation of some of the thickenings which are generally used, while those employed in special cases will be described when treating of the colours for which they are required. The thickenings only react in a mechanical way by keeping the colours on the spots for which they are intended, and preventing them from running. They must neither be too thin nor too thick, or else patterns with definite and sharp outlines will not be obtained. For the convenience of those conversant with French (metrical) weights and measures, and also for the convenience of practical men, the proportions are given both in metrical weights and measures and also English units, the first calculated of course by grammes and litres, and the second by gallons and pounds.

1 litre is divided into 1,000 cubic centimeters (cc.), and weighs 1,000 grammes.

1 gallon weighs 10lb.

PREPARING THICKENINGS.

Gum Solution.

No. 1.—For ordinary laboratory work.

600 grs. gum arabic	6lbs.
1,000 ,, boiling water	1 gal.

Na. 2.—Thicker.

1,000 grs. gum arabic	10lbs.
1,000 cc. boiling water	1 gal.

No. 3—Very Thick.

1,500 grs. gum arabic	15lbs.
1,000 ,, water	1 gal.

The gum is added into the boiling water, and the whole is stirred by a wooden stirrer until well dissolved. By heating gently the solution is hastened. When all is dissolved it is left to cool and settle, then strained or sieved, and kept in bottles or covered vessels for use. The straining is generally done by hand, or by means of sieves having wire gauze at the bottom, the colour being made to go through by pressing gently with a brush.

Starch Paste.

No. 1.—A very useful paste for laboratory work.

100 grs. wheat starch	1lb.
1,000 cc. water	1 gal.

The water is mixed with starch quite cold. If no steam is available, the boiling is performed on the gas or on free fire. If not much of this thickening is required it is better to prepare it fresh every time by taking

200 c.c. cold water.
20 grs. wheat starch.

Put together in an enamelled iron vessel (saucepan with handle) and stir well by means of a wooden spatula. Then heat on an ordinary Bunsen burner, and bring up to the boil. Stir well all the time, taking care that the spatula reaches the bottom of the saucepan, so as to prevent burning. Boil five or six minutes, then remove from the gas, and cool by putting the vessel in cold water. Stir all the time, and when quite cold it is ready for mixing. When the starch is of good quality a very good thickening is obtained in a few minutes. On the large scale some practice is required before a good thickening is made.

No. 2.—*Starch Thickening* (thick).

1,000 cc. water	1 gal.
150 grs. starch	1½lbs.

in boiling small quantities at a time it is rather difficult to obtain a good thickening, as the water evaporates too quickly in proportion, therefore for small experiments it is better to reduce the amount of starch to 120 or 130 grs. to the litre of water.

Dextrine (artificial gum) *Water.*

1,000 grs. gum artificial (Dextrine)	10lbs.
1,000 cc. boiling water	1 gal.

Stir, it will dissolve easily without further heating.

Tragacanth Mucilage.

100 grs. tragacanth	1lb.
1,000 cc. water	1 gal.

The gum is mixed with the water and left to soak all night, then it is heated on the water bath (or in the steam cased pans) for at least 12 hours. The water which evaporated is replaced, so as to keep the whole to the same volume and weight. On a small scale it is very difficult to obtain a good tragacanth water or mucilage, except by very long heating on the water bath—sometimes even two or three days. The water which evaporates is constantly replaced in order to obtain the same volume and weight.

Albumen Water.

1,000 grs. egg albumen	1lb.
1,000 cc. cold water, or at most 30-35° C. about 100° F.	1 gal.

Mix, leave to stand about 12 hours, stir occasionally and sieve from the insoluble.

Blood Albumen.

900 to 1,000 grs. blood albumen	14oz. to 1lb.
1,000 cc. water (cold)	1 gal.
200 grs. arsenite of soda	2 lbs.
or turpentine to prevent putrefaction.	

For small experiments the white of eggs can be used at once. The egg is broken and the white (which is albumen) is carefully separated from the yellow, and can be used immediately for the printing, and gives good results.

As is well known, the solutions of both egg and blood albumen are very liable to decomposition, as they easily putrefy, and therefore it is advisable to prepare them always fresh. These solutions are also very liable to occasional frothing, when printed on the machine for this purpose; turpentine is therefore added, which acts in a certain sense both to prevent putrefaction and to do away with the frothing. Arsenite of soda is also used to prevent putrefaction, as already explained. In preparing the solutions of albumen, the following plan can be recommended :—The crystallised arsenite of soda is dissolved at the boil in the necessary amount of water, and when the solution is cooled down to about 30° C., the albumen is stirred in by means of a wooden spatula, the whole being repeatedly agitated, and then left to settle and preferably sieved.

A good fixing solution is made by dissolving

300 grs. egg albumen	3lbs.
300 grs. blood albumen	3lbs.
1 litre water	1 gal.

Colours fixed by the above solution stand soaping better than those fixed by means of blood albumen alone. In dissolving, the albumen should always be added to the water, and not the reverse, and the whole constantly stirred in order to prevent the particles of albumen from sticking to each other.

There are other albuminoid substances which are used for the fixing of pigments, such as caseine, or more commonly known as lactarine, and gluten, but they are not very extensively employed. As a rule caseine is dissolved in ammonia, and the colours, after printing, are fixed by steaming in the same way as with albumen, but the shades obtained are not so fast as those obtained with albumen, neither do they come up to them in brilliancy.

Special thickenings will be mentioned when describing the different printing or rather fixing methods, when the preparation of the different mordants and fixing agents will be indicated.

PREPARATION OF MORDANTS.

In some cases it is to be recommended that these mordants should be prepared in the laboratory and the print-works, not only on account of the saving that could be made on them, but principally in order to have reliable material of well-known strength to work upon. The most important of these mordants is the acetate of alumina, which is prepared by two distinct methods: either by double decomposition of the sulphate of alumina or alum with the acetate of lead, when the insoluble sulphate of lead is thrown down, and the acetate of alumina is obtained in solution, and separated from the other by filtration; or the hydrate of alumina is precipitated from a sulphate of alumina or alum solution, by means of soda, and the precipitate washed, passed through a filter press and dissolved in acetic acid. Both methods yield good results, either for the preparation of acetate of alumina, or of acetate of chrome, the raw material for the latter being the chrome alum now so extensively found in commerce.

ACETATE OF ALUMINA.—The proportions of alum or sulphate of alumina and lead acetate vary a great deal, according to the different authors. As a rule, equal quantities of alum and acetate of lead, or of the latter and sulphate of alumina can be taken, using water sufficient to obtain the desired strength, but the following recipes may be taken as examples.

In all cases it must be observed that it is not advisable to use a larger proportion of the lead salt, as it would only be wasted, while even if the amount of alum or sulphate of alumina should be in excess of the sugar of lead this will not be a disadvantage, especially in preparing a mordant for alizarin red dyeing.

Acetate of Alumina No. 1, *about* 6° *Bé. or* 9° *Tw.*

50 grs. alum or sulphate of alumina	5lbs.
dissolved in	
200 cc. boiling water	2 gals.
In another vessel	
50 grs. acetate of lead dissolved in	5lbs.
150 cc. boiling water	1½ gal.

When both solutions are ready they are mixed, the whole well agitated and left to settle, then filtered and made up to a regular strength, say 5° or 6° Bé., either by adding water, or by the addition of the washings obtained from the sulphate of lead (precipitate), which still contains some acetate of alumina adhering.

This acetate of alumina gives good results in alizarin and turkey red dyeing, made up at about 4° to 5° Bé. (6° to 9°Tw.)

But equally good results are obtained for plain alizarin dyeing by the following :—

Acetate of Alumina No. 2.

50 grs. alum	5lbs.
dissolved in	
200 cc. boiling water	2 gals.
In another vessel	
40 grs. acetate of lead dissolved in	4lbs.
150 cc. boiling water	1½ gals.

Both solutions are well mixed, it is then filtered, the precipitate washed by little water, and the liquor made up to about 4° to 6° Bé. (6° to 9° Tw.)

In order to obtain good reds it is necessary that either the alum or the sulphate of alumina should be free from iron; this is easily ascertained by testing a solution of either with a solution of ferrocyanide of potassium, which will give a blue colouration if iron is present.

These two acetate of alumina solutions will be found also useful for the printing of colours for which no very deep shades are required; for this purpose they are taken instead of the water in the preparation of the starch paste, for instance :—

Starch Paste with weak Acetate of Alumina.

100 cc. of acetate of alumina 6° Bé (9° Tw.)	1 gal.
7½ to 10 grs. wheat starch	¾ to 1lb.

Mix cold, then boil, and stir until cold, and a paste will be obtained which will be found very useful for the fixation of all colours which form insoluble lakes with alumina. Or the acetate of alumina is simply thickened by means of British gum.

This acetate of alumina starch paste will be found also useful for printing patterns on calico which, after ageing and dunging, can be dyed in alizarin, or other colouring matters, but the shades obtained are not so deep as those produced when a stronger acetate of alumina is employed.

The following mordant is much stronger, and will be found useful for steam and dyeing alizarin styles.

Acetate of Alumina of about 14° *Bé.* (22° *Tw.*)

100 grs. sulphate of alumina or alum	10lbs.

Dissolved in

180 cc. boiling water	1¾ gal.

And when the solution is complete add

100 grs. acetate of lead	10lbs.

Boil until latter is dissolved, stir well, leave to settle, filter, wash, precipitate, and make liquor up to 14° Bé. (20° to 22° Tw.), by adding water if necessary.

Basic Acetate of Alumina, 15° *Bé.*

In 1000 cc. (1 litre) water, dissolved at the boil.	1 gal.
750 grs. alum	7½lbs.
650 grs. acetate of lead	6½lbs.

When still lukewarm add carefully

50 grs. soda crystals	½lb.

Stir until latter is dissolved, leave to cool, filter, wash and make up to 15° Bé.

Another mordant, giving similar results to the above, but principally useful for printing, is the following :—

Acetate of Alumina, 14° *Bé.* (20° *to* 22° *Tw.*)

In 1000 cc. (1 litre) boiling water	1 gal.

dissolve

500 gr. alum,	5lbs.
400 gr. acetate of lead.	4lbs.

Stir until all dissolved, then leave to settle, filter and make up to above strength. As will be easily seen these stronger mordants are prepared in the same proportions as the weaker ones, only less water is used in dissolving. In making up these mordants it is always well to keep to a regular strength, either by the Bé. or the Tw.,* or better, by estimating the amount of alumina in the mordants. In making the standard mordants, if working with the Tw. hydrometer, as it is generally the use in this country, it is well to keep two simple strengths, for instance, in the case of the weaker mordants it is well to make them always, say at 8° or 10° Tw., and the stronger at about 20° Tw. The other method of preparation of the acetate of alumina is the following:—The hydrate of alumina, or rather a basic sulphate of alumina, is thrown down by means of soda, and the precipitate is filtered, pressed, and dissolved in acetate acid.

Basic Sulphate of Alumina.

80 grs. alum	4lbs.
dissolved in	
200 cc. boiling water	1 gal.
In another vessel	
70 grs. soda crystals	$3\frac{1}{2}$lbs.
are dissolved in	
200 cc. boiling water	1 gal.

When both solutions are almost cold the soda is added to the alum liquor, and the basic alumina sulphate is precipitated, washed by decantation several times, filtered, and pressed.

Acetate of Alumina, 15° *Bé.* (22° *Tw.*)

100 grs. of above pressed alumina	10lbs.
are dissolved in	
30 cc. acetic acid at about $7\frac{1}{2}$° Bé (10° Tw.)	3lbs.,

and made up to above strength.

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* At the end of this book will be found a comparative scale of the Beaumé and Twaddle degrees, and respective specific gravity.

There is a preparation in commerce which goes under the name of alumina, and another product known as carbonate of alumina; both give very good acetates of alumina, by being simply dissolved in acetic acid. The solution is performed either in the cold, and is completed in some cases only after several days, or at a gentle heat. To obtain acetate of alumina with the so-called dry alumina, take

100 grs. dry alumina	10lbs.
350 cc. hot water	3½ gals.
200 cc. acetic acid	2 gals.

Sulphocyanide of Alumina, 30° Tw.

In

1000 cc. (1 litre) boiling water	1 gal.

dissolve

650 grs. sulphate of alumina.	6½lbs.

then add

850 grs. sulphocyanide of barium	8½lbs.

Stir until dissolved, leave to cool, filter, and make up to 18 to 20° Bé.

Nitrate of Alumina, 15° Bé. (22° Tw.)

In

1000 cc. boiling water	1 gal

dissolve

500 grs. nitrate of lead, and	5lbs.
500 grs. alum.	5lbs.

Mix until dissolved, leave to settle, cool, filter, and make up to strength.

After alumina mordants, the next in importance, as far as printing is concerned, are the iron and chromium preparations. Here again the acetates occupy the most important position, although in some cases the nitro acetate, or the nitrates and the sulphocyanides are employed.

Acetate of Iron is found in commerce in large quantities, and is manufactured on a large scale principally by the reaction of raw acetic acid or pyrolignous acid on iron filings or scrapings. It is sold as a concentrated liquor, and only requires to be diluted to the necessary strength with water before use. It is also occasionally prepared in the print works or in the laboratory, either by the above method or by double decomposition of the copperas with either acetate of lead (brown sugar of lead) or more cheaply with acetate of lime, or by precipitation of the carbonate of iron by means of soda from a copperas solution, and then dissolving in acetic acid in the same way as mentioned before for the acetate of alumina, etc. The following recipes may serve as examples.

Acetate of Iron, 20° *Bé.—No.* 1.

450 grs. boiling water .... 1 gal.
dissolve
275 grs. copperas .... 5½lbs.
and then add
275 grs. acetate of lead .... 5½lbs.

Boil and stir until dissolved, and then leave to settle and filter from the sulphate of lead, make up the liquor to 20° Bé. (about 30° Tw.)

If a weaker mordant is required, more water is taken either for the dissolving or for the washings of the sulphate of lead, and washings are added to the liquor.

Acetate of Iron, 10° *Bé.—No.* 2.

In 1 litre (1,000 grs.) boiling water .... 1 gal.
dissolve
200 grs. copperas .... 2lbs.
Then precipitate with about
140 grs. ammonia of 0·9 sp. gr...................... 1¼ to 1½lbs.

Leave to settle, wash by decantation two or three times, filter, wash precipitate, or filter several times until washings do not give any more precipitate with chloride of barium, then leave to drain, or press, when about 1,500 grs. of hydrate of iron will be obtained.

To prepare the Acetate.

Dissolve the above precipitate in acetic acid in the following proportion; for

250 grs. precipitate .... 2½lbs.

take

1 litre acetic acid, 6° Bé (9° Tw.) .... 1 gal.

After the solution is effected make up the liquor to 10° Bé (15° Tw.), with water.

Instead of the ammonia, soda can be employed for the precipitation as in the following recipe.

Acetate of Iron.—No. 3.

In 1 litre boiling water .... 1 gal.

dissolve

500 grs. copperas .... 5lbs.

then precipitate carefully with about

200 grs. soda ash of 98 per cent. .... 2lbs.

dissolved in

1 litre hot water .... 1 gal.

Filter, wash or filter several times, leave to drain and dissolve in

750 grs. acetic acid 6° Bé. .... 7½lbs.

Make up to the desired strength with water. This method is more economical than the preceding one.

It must be observed that in the filtration of the precipitates, the filter presses will be found of great utility, as they will save much trouble and labour.

Nitrate of Iron, 40° *Bé. (about* 75 *Tw.)*

In 1 litre boiling water .... 1 gal.

dissolve

1,000 grs. nitrate of lead ... . 10lbs.

1,000 grs. copperas .... 10lbs.

Leave to settle and filter; if a weaker mordant is required then use more water.

Sulphocyanide of iron is rarely employed, but, if required, can be prepared by double decomposition between the sulphocyanide of barium and copperas. *Nitro acetate of iron* is sometimes used, and can be prepared either by mixing some of the acetate with the nitrate mordant, or by double decomposition with acetate of lead along with the nitrate and copperas. In some cases iron alum is used for the preparation of the iron mordants, though very seldom.

Acetate of Chrome, 10° *Bé.* (15° *Tw.*)—*No.* 1.

In 1 litre boiling water	1 gal.
dissolve	
300 grs. chrome alum	3lbs.
then add	
300 grs. acetate of lead	3lbs.

Stir until dissolved, leave to settle, and filter and make up the liquor to 10° Bé. If a stronger mordant is required, either less water is used or the above mordant is concentrated by evaporation, say up to 18° or 20° Bé.

Acetate of Chrome, 16° *Bé.* (25° *Tw.*)—*No.* 2.

In 1 litre of boiling water	1 gal.
dissolve	
1,300 grs. chrome alum	13lbs.
then add	
1,300 grs. acetate of lead	13lbs.

Leave to settle, etc. In the preparation of the acetate by double decomposition, it must be borne in mind that, especially when the mordant is very strong, a certain quantity is still left with the precipitate, and would cause a loss if not recovered. As a rule the precipitate is always washed once, several times if necessary, and the washing either used in the preparation of the next mordant, or for dilution of the same. Acetates of chrome are found on the market in large quantities and at moderate price, since they are produced on a large scale. They are manufactured by different methods, but principally by treatment of the chrome alum solution with soda, and dissolving the precipitate in acetic acid, as for instance :—

Acetate of Chrome, 16° *Bé.* (25° *Tw.*)—*No.* 3.

In 1 litre boiling water .... 1 gal.
dissolve
200 grs. chrome alum.............................. 2lbs.
and precipitate by carefully adding the solution of
64 grs. soda ash .... 11oz.
in
250 grs. water .... 2$\frac{3}{8}$lbs.
Filter, wash the precipitate, and drain or use the filter press. Yield about
300 grs. paste.. 3lbs.
which is dissolved in
140 to 150 grs. acetic acid.. .... 1$\frac{1}{2}$lbs.
and gives a mordant of about 16° Bé.

Acetate of Chrome.—*No.* 4.

In 1,000 grs. (1 litre) acetic acid, 6° Bé .... 1 gal.
dissolve at the boil
100 grs. bichromate of potash .... 1lb.
Then add
50 grs. brown sugar .... $\frac{1}{2}$lb.
and continue the boiling until the solution does not give any more yellow precipitate with a solution of acetate of lead. Make up the solution to 20° Bé. (30° Tw.)

Nitrate of Chrome, 20° *Bé.* (30° *Tw.)*

In 1,000 grs. (1 litre) water .... 1 gal.
dissolve at the boil
300 grs. chrome alum................................ 3lbs.
250 grs. nitrate of lead .... 2$\frac{1}{2}$lbs.
Leave to settle, filter, and make up the liquor to 20° Bé

Nitro Acetate of Chrome, 10° *or* 12° *Bé.—No.* 1.

In 1 litre boiling water	1 gal.
dissolve	
500 grs. chrome alum	5lbs.
and	
100 grs. acetate of lead	1lb.
and	
100 grs. nitrate of lead	1lb.

Leave to settle, filter, and make up to 10° or 12° Bé. (about 15° Tw.)

Nitro Acetate of Chrome, 30° *Bé.—No.* 2.

In a stoneware pot or enamelled iron vessel add—

1 litre boiling water	1 gal.
in which dissolve	
500 grs. bichromate of potash	5lbs.
then add	
580 grs. nitric acid	5lbs. 14ozs.
and then carefully, and in small portions at a time,	
100 grs. glycerine	1lb.
and finally add	
1 litre acetic acid	1 gal.

It will be easily understood that either bichromate of potash or bichromate of soda can be employed. These products can now be found on the market in large quantities, and in many cases of excellent quality. For some special purpose the sulphocyanide of chrome is used, in the print-works principally, for the preparation of colours for logwood steam blacks, and it is preferred by some printers and colour mixers. It can be bought ready made in a moderately concentrated solution, but it can also be easily prepared, by those who prefer to make their own mordants, in the same way as the alumina sulphocyanide is prepared, viz.—by the double decomposition of the barium salt with the chrome alum, as for instance :—

Sulphocyanide of Chrome.

In 1 litre boiling water	1 gal.
dissolve	
500 grs. chrome alum	5lbs.
then add	
500 grs. sulphocyanide of barium	5lbs.

Stir well, leave to settle, filter, and make up the liquor to 15° Bé., or according to requirement. 20 to 22° Tw.

Chlorate of Chrome, 15° Bé. (22° Tw.)

This product, although not largely employed, is still of some use in special cases, and can be prepared as follows:—

In 1000 grs. water	1 gal.
dissolve at the boil	
300 grs. chlorate of barium	3lbs.
and then add	
225 grs. chrome alum in fine powder.	2¼lbs.

Stir well, then leave to settle, filter. The chlorate of alumina, which is also very useful for special purposes, can be prepared in a similar way.

Basic Chlorate of Chrome.

To the above preparation, while still hot, and before filtering, add

75 grs. precipitated hydrate of chrome	¾lb.

leave for 12 hours, occasionally stirring, then filter and make up to about 16 or 18° Tw.

On account of the chlorate of barium being expensive, the chromium chlorate thus prepared is rather dear. A cheaper method is the following:—

Chlorate of Chromium, No. 2.

Dissolve	
60 grs. chrome alum	7½lbs.
in 80 ,, boiling water	1 gal.
and precipitate with a solution of	
20 grs. soda (98 per cent.)	2½lbs.
in 80 ,, water	1 gal.

wash, precipitate with warm water, or filter; leave to drain, and dissolve in about

10 grs. sulphuric acid, 66° Bé.	1¼lbs.

taking care that there is an excess of the chromium hydrate undissolved, in order to have it free from acid. After filtering mix the solution with another solution of

22 grs. chlorate of potash	2lbs. 10oz.
in 50 ,, water	½ to ¾ gal

leave to stand for a few days in a cool place, when the sulphate of potash crystallises out.

The liquor after filtration will contain the chromium chlorate, with a certain amount of sodium sulphate; but if potash is used instead of soda in the precipitation of the hydrate, the greater part of the potassium sulphate will crystallise out.

As will be easily seen from the above recipes, the chromium preparations are rather numerous, and they are certainly very useful, and largely employed in calico printing.

There is another class of metallic mordants which has attracted, in the last two or three years, considerable attention, and which will, no doubt, be capable of more extended and useful applications in the future, these products can be distinguished under the general name of ALKALINE MORDANTS.

The alkaline mordant of alumina, or aluminate of soda, although known for years, has not been very largely employed, except in the last few years, for the production of plain dyed alizarin reds, but it has been a long time used for the production of madder pinks, though the other alkaline mordants, especially the chrome, and to a certain extent also the iron alkaline mordants, are of quite recent application. As these mordants will be found very useful in special cases I will here give their methods of preparation, which it will be seen are very simple. For instance—

Aluminate of Soda.

Alum or sulphate of alumina are dissolved in boiling water, and then precipitated by means of soda, as explained before when treating of the preparation of acetate of alumina, and the pressed alumina is dissolved in caustic soda according to requirement.

Aluminate of Soda, 20° Bé. (30° *Tw.*)

In 1 litre of caustic soda lye at 36° Bé. (65° Tw.)...1 gal.
dissolve as much of the pressed hydrate of alumina as it will take; about
1200 or 1400 grs. alumina ....12 to 14lbs.
Leave to settle, and, if necessary, filter: make up to 20° Bé., (30° Tw.) when the liquor is ready for use,

Chrome Alkaline Mordant.

2 parts acetate of chrome 10° Bé. (15° Tw).
2 ,, caustic soda lye 36° Bé. (65° Tw.)
1 ,, water.

Mix in the cold. A stronger mordant can be obtained by taking a stronger chrome acetate and less water with the caustic soda.

Iron Alkaline Mordant.

2 parts nitrate of iron.
2 ,, caustic soda 36° Bé. (65° Tw.)
1 ,, glycerine.

This latter is especially useful for buff shades. The following modification has been found to answer very well in practice:—

20 parts nitrate of iron 30° Bé. (52° Tw.)
60 ,, glycerine.
20 ,, ammonia.

The nitrate of iron is first mixed with the glycerine, and then ammonia is added; the clear solution can be kept in bottles for use.

Both the iron and the chrome alkaline mordants have the desirable property of fixing the respective metallic oxides on the fibre, if cotton goods are immersed in a bath properly prepared with these mordants diluted with water, and afterwards exposed to the air. The same mordants properly thickened will also be found useful in printing. Of the other mordants or preparations used in printing the following ought to be mentioned here; the other minor productions which are only employed for special purposes, will, if necessary, be mentioned when dealing with the fixation of the different colours.

Acetate of Lime, 15° *Bé.* (22° *Tw.*)

100 grs. of burnt lime	10lbs.
are slacked with	
250 cc. water	2½ gals.
and mixed with a solution of	
400 cc. acetic acid	4 gals.
in	
200 cc. water	2 ,,

Or the ordinary acetate of lime of commerce can be taken and dissolved in water in proportion to the strength required, but the product will not be so pure.

Nitrate of Calcium.

50 grs. lime	5lbs.
slacked with	
200 cc. water	2 gals.
then add	
180 grs. nitric acid 36° Bé. (66° Tw.)	1¾ ,,
diluted with	
150 grs. water	1½ ,,

Mix cold; leave to settle and filter, and make up to 15° Bé. (22° Tw.), with water if necessary.

Acetate of Tin, 14° *Bé. (about* 20° *Tw.)*

In 1 litre boiling water	1 gal.
dissolve	
750 grs. tin salt	7½lbs.
and	
1000 grs. acetate of lead	10lbs.

Leave to cool and settle, then filter and make up to above strength.

Acetate of Manganese, 30° *Bé. (about* 50° *Tw.)*

Dissolve in

150 grs. manganese chloride 36° Bé	1 gal.
100 grs. acetate of lead	7lbs.

Leave to settle, filter, and make up to 30° Bé.

Manganese Acetate.—No. 2.

In 1 litre boiling water	1 gal.
dissolve	
500 grs. manganese chloride	5lbs.
and	
480 grs. acetate of lead	4¾lbs.

STEAM COLOURS.

FIXING PIGMENT COLOURS.

These come in the market either as a paste or as dry powders: but some principally in the paste form, such as chrome yellows, oranges, etc., while others are principally sold in powder form, such as ultramarine, vermilion, etc. One of the most important requirements of the pigment colours is that they must be in very fine state of division and absolutely free from gritty substance, which is the cause of many troubles. A ready method of ascertaining if a pigment colour has been ground finely enough is the following: If the pigment is already in the paste form, then by rubbing some of the paste between the fingers, it is felt at once if it is free from grit or not, while to see if it is fine enough some of the paste is rubbed, by means of the finger, on a glass plate, and by looking through the spot thus formed (holding the glass plate against the light), it can be easily seen if the colour is finely powdered or not. It can be easily judged also by smearing a little of the pigment colour on white paper with the finger. If the pigment is bought in the form of a powder, then it will have to be mixed with water and rubbed as above, either on glass or paper, or on a white porcelain plate.

A ready method of ascertaining the different shades and strengths of two pigments in the dry state, such as, for instance, two qualities of ultramarine, is the following: Place some of the standard samples of ultramarine on a white paper, and lay on the colour a glass plate, and by means of a knife or spatula place a little of the other sample in the middle of the flattened ultramarine standard sample; flatten the whole again gently by means of the glass plate, when the difference of the two samples will be strikingly apparent. This method has already been alluded to, and if it is mentioned here again, it is because it will facilitate the descrimination of pigment samples, and give an idea before proceeding with the printing tests.

But the most reliable method of testing these pigment printing colours is by printing them on the roller printing machine, side by side, and judging by the difference of the colour of the prints thus obtained. In many printworks the pigments are ground on mills before use, so it must be observed that the colours ought to be tested after grinding, or if they are tested before they must either be ground in the mortar or in a small laboratory mill before printing, in order to ensure reliable results.

The pigment colours now generally used are the following: First in importance is *Ultramarine*, then *Chrome orange*, *Chrome* and *Cadmium yellow*, Guignet's or *Chrome green*, *Vermilion*, *Buff* or oxide of iron, *Ochre*, *Burnt sienna*, *Lampblack*, etc. The ultramarine is found in the trade of different qualities and consequently of different prices; it is sold sometimes even as a paste, which has been previously ground with glycerine in the proportion of 5lbs. ultramarine and 3lbs. glycerine of 25 to 28° Bé. If, instead of glycerine, the ultramarine is ground with olive oil, the colours thus obtained are stated to give a deeper shade.

The following proportions can be taken for printing experiments and even trials on a large scale—

20 grs. ultramarine	1lb.
20 ,, albumen solution	1lb.
20 ,, gum solution	1lb.

In the preparation of the different colours for printing, the following remarks will be found useful: The vessels which are suitable for mixing the colours are principally porcelain capsules, or small enamelled iron dishes or glass beakers; but the porcelain capsules are preferable because they are light, easily handled and cleaned. The mixing vessel is put on the scale, weighed, and then the different ingredients added one by one, and of course also carefully weighed. For the stirring and mixing of the colours wooden spatulas are preferable to glass ones, although the latter ones will be found useful if properly made; in some cases also porcelain spatulas can be employed; but for all ordinary purposes there is nothing better than a wooden spatula, which anyone can make by means of a penknife. Sometimes, instead of weighing the standard solutions or thickenings in the mixing of the colours, these are all taken by measure; for this purpose those glasses employed by apothecaries, and divided into ounces, ¼oz. and ½oz., will be found very convenient; but if no such graduated glass is at hand, then it is very easy to graduate either beakers or glasses, or tallboys in simple proportions, say a beaker holding over 100 ccs. can be graduated in divisions of 10 ccs. each, etc. It is very convenient to have always graduated glasses at hand for mixing colour experiments for printing, as they save a lot of trouble and time.

The colours once mixed must as a rule be well strained before printing. This is performed either by hand by means of a piece of clean calico, the texture of which is neither too close nor too open, or by means of a silk or metallic sieve placed at the bottom of a tin ring, the colour being made to pass through the sieve by pressing on it by means of a brush.

The colour having been duly mixed, we can proceed to the printing, or rather to the testing by printing. To begin with, the tests are simply comparative, that is, comparison is made between the shade obtained and that of a standard sample or a sample of well known quality.

Of course the price of the two or more pigments must be taken into account. Suppose the standard sample of a colour is bought at 6d. per pound, and another sample is offered at 4d. per pound, then in mixing of the testing colours we have to calculate the amount of the pigment in inverse proportion to their price; for instance, by taking the above proportions for the mixing of the printing colours, as an example, we would take 20 grs. of the standard pigment; now, taking them in inverse proportion to their prices we would have:—

$$\text{Sample at 4d} : 6d. = 20 : x = \frac{120}{4} = 30;$$

that is, that of the cheaper pigment we should have to use 30 grs., while at the standard we would take 20 grs. Now we have another thing to consider. As a general rule, in preparing colours to be tested by printing against each other, we must have the same amount of both samples, by weight or by measure, of the thickened colours; therefore, if we were to take, for instance, for the standard—

20 grs.	pigment.	2lbs.
20 ,,	albumen	2lbs.
20 ,,	gum solution	2lbs.
60 grs,		6lbs.

and for the sample at 4d. to be tested—

30 grs.	pigment	3lbs.
20 ,,	albumen	2lbs.
20 ,,	gum solution	2lbs.
70 grs.		7lbs.

we should not have a fair test, the amounts not being the same in both; therefore by adding another 10 grs. of gum solution to the standard colour we bring it up to 70 grs., the same as the other sample. This rule, therefore, will have always to be followed — that the printing colours obtained by two or more samples which are to be tested must always be the same weight, or contain the same volume, if they have been mixed in the same proportions.

The above proportions of thickening and pigment must not be taken as absolute, as they can be varied according to the colours to be tested, and to the shade required. All pigments, both in paste form or in dry powder, can be tested by this method, and by following approximately the above proportions; but if the pigment paste be rather weak, its proportion can be increased, and the proportion of gum solution diminished, at the same time making it stronger;

for instance, the following proportions could be taken for a pigment paste—

30 grs.	pigment paste	3lbs.
10 ,,	gum solution (N2 or N3)	1lb.
20 ,,	albumen solution	2lbs.

In preparing the colours for printing, it will be found of advantage to adopt the following plan before printing: A drop of the thickened colour is applied on a piece of white calico or a sheet of white blotting paper, with the hand, when the spot of the colour is pressed through the fabric, and gives a pretty good idea of the intensity of the shade that will be produced; in case it should be too weak, more pigment colour could be added, and if it should be too deep it can be diluted by adding more thickening.

The printing of the prepared colours is performed either by means of the blocks or by means of the roller printing machine; in the first case, care must be taken that the blocks take equal parts of the testing colours, while if printing on the machine care must be taken that the pressure be evenly distributed in the same way all over the roller, in order to have as fair results as possible. Both with the block and the machine, with a little practice, good results will be obtained if the operations are carefully performed; and this is more difficult to describe than to execute.

The following recipes may be taken as further examples of printing pigment colours on a large scale, for which very often no further thickening is employed than the albumen or blood albumen solution :—

Guignet's Green (Chrome Green).

100 grs.	albumen solution 50 per cent.	1 gal.
60 to 70 ,,	green pigment	6 to 7lbs.

Black.

100 grs.	blood albumen	1 gal.
50 ,,	gum tragacanth solution	½ gal.
60 to 70 ,,	pigment black	6 to 7lbs.

This black, if diluted with more thickening, gives a grey; the same effect is obtained if the amount of black pigment is reduced in the above recipe.

Slates can be produced by mixing the grey colours with a certain amount of ultramarine in varying proportion, according to the shade required.

Other compound shades, such as browns, chocolates, olives, &c., are either obtained from pigments already sold in the market, or are produced by mixtures of the ordinary colours.

FIXING COAL TAR COLOURS.

These dyestuffs now form the most important class of dye products which are used in printing, and we will, therefore, devote some attention to the methods of their employment, which methods are similar to those employed in the testing.

For calico printing, the aniline and the anthracene colours are of the utmost importance, while those derived from naphthalene, principally the azo colours, are only employed to a moderate extent in printing, on account of the difficulty or even impossibility of obtaining fast shades with these products. The aniline colours are divided into basic and acid colouring matters; the basic products are those which are neutral salts, the combination of an acid with the base of the dyestuff itself; for instance, magenta is a basic colouring matter, and is the combination of the base of the dyestuff (rosaniline) with hydrochloric acid. The methyl violet also is a basic colouring matter, and is also the combination of hydrochloric acid with the base. The other basic colours are methyl and malachite green, the phenyl rosaniline blues (the aniline blues, soluble in spirit but insoluble in water), induline soluble in spirit, auramine, methylene blue, etc.

While the acid colours are those which have been obtained by reacting on the bases of the aniline colours by means of sulphuric acid, and are in fact sulpho acid derivatives of the basic colours, and they are generally brought into the market in the form of ammonia or soda salts of these sulpho acids, acid colours, for instance, alkaline or Nicholson (soluble) blues, azo oranges, scarlets, etc. As a general rule much faster shades are obtained by means of the basic aniline colours, and these are also much more employed in printing than the acid colours.

It will be remembered that in cotton dyeing the methods of fixation vary accordingly, as the dyestuff be of basic or acid character, and the difference of methods of fixation of aniline colours is even more striking in printing. Here also it must be observed that the methods of fixation can be employed, not only for single colours, but to groups or classes of colouring matters; for instance, the basic aniline dyestuffs can all be employed by the same methods. It will be remembered also that magenta, violets, greens, etc., can all be employed on cotton which has been mordanted with tannic acid or sumach, and tin or tartar emetic; now all these dyestuffs can be also employed in printing by a method relying on the use of tannic acid or sumach extracts. The principle is in the main identical with that followed in the fixation of these products in dyeing, only the manipulations being different. For instance, in dyeing the fixation of these dyestuffs relies on the principle of forming an insoluble lake on the fibre, consisting of the combination of the tannic acid with the colouring matter, and the metallic compounds of tin or of antimony. This principle of the formation of coloured insoluble lakes is also followed in printing, and tannic acid is also used for its fixation. A method generally followed of fixation, and of testing basic aniline colouring matters, relies therefore on the employment of tannic acid. A colour is formed consisting of thickening, the solution of colouring matter and acetic acid. The acetic acid is added in the preparation of the colour in order to prevent the tannic acid from combining with the dyestuff, in other words the acetic acid keeps both the colouring matter and the tannin in solution in the thickened colour, and prevents their combining with each other; but when the colour is printed and the cloth is dried and steamed, the acetic acid is expelled, and the colouring matter and the tannin then go into combination to form the insoluble coloured lake. This lake, however, not being sufficiently fast to stand by itself, a metallic mordant is necessary to give additional fastness to the colours; for this reason the cloth, after printing, drying, and steaming is passed into a solution containing tartar emetic. The antimony of the tartar emetic enters into combination with the tannin, and the colouring matter already partially fixed on the fibre and a coloured lake of the tannate of antimony, and the colouring matter is formed. This lake is not very easily attacked by soap, and therefore the shades thus produced are pretty fast against soaping. Having explained the principle of the fixation of the majority of the basic aniline colours, we will now proceed to describe the practical manipulations.

To begin with, we require to prepare the solution of the colouring matters. As a rule the aniline, and generally the coal tar colours, are sold in the form of a powder or as crystals, at all events in the solid form, and they will have to be dissolved before use. In some cases they are sold in the form of a paste, as it is sometimes the case with aniline blue, which is brought in the market under different names, such as gentiana blue, cerulean blue, etc. In some instances also the colouring matters are brought in the market in solution. When the aniline colours are bought in the dry state they have to be dissolved. Water, of course, is the cheapest and the most convenient of all solvents, but in some instances the product is not soluble in water in such proportion as to give a deep shade, and in this case another solvent has to be employed. Alcohol can be used with advantage in some cases—in this country methylated spirit being generally employed; in some special instances glycerine can be resorted to, while acetic acid forms a valuable and also comparatively cheap solvent for some aniline colours.

The methyl violets, methyl greens, malachite, or bitter essence green, methylene blue, etc., can be readily dissolved in hot water, and the solutions (if not made too strong) will also keep well after cooling. A convenient amount of colouring matter to dissolve, in the case of the above products, is 5 parts of colouring matter in 100 parts of hot water; the solution is left to cool, and then filtered. Some aniline colours, such as magenta, would not keep completely in solution if dissolved in the above proportion, and it will be mentioned in each case separately how the solution is made. It must be observed here that it is customary in printworks to keep standards, and in the case of colouring matters, standard solutions of the different products. These standard solutions, which are prepared always in the same proportions, are always prepared in pretty large quantities at a time, and kept ready for use. In the laboratory it is always best to prepare the standard solutions fresh, or at all events at short intervals. In the case of aniline colours especially, there is no difficulty in keeping the powders of the different dyestuffs in well corked bottles, and little trouble in making the solutions fresh every time, this being a more accurate plan than preparing standard solutions of the colouring matters, and keeping them in stock for a long time. This rule applies more especially in the testing of the different dyewoods or dyewood extracts with each other, as some of them are apt to ferment, or at all events to deteriorate, if kept long in stock. In case of dyewood extracts, it is also well to renew the standard samples now and again, as some of the extracts get spoiled by long standing.

There is also another observation which is worth making. In the testing of dyestuffs, both in dyeing and by printing, some chemists adopt the following plan:—The standard samples are dyed or printed in different proportions, and the patterns are posted in a book with the report of the amount of colouring matter used in each case; in this way a scale of dyed or printed patterns is obtained, going from light to deep shades, and passing through the intermediate hues. For instance, in the case of dyed patterns with any dyestuff, such as magenta, several patterns are dyed; to begin with, a very light shade, one pattern with 0·1 per cent. colouring matter, standard sample, other patterns following, 6·2 per cent., 0·3 per cent., and so on up to 0·9 per cent. and 1 per cent. If a sample has to be tested against this standard, then a pattern is dyed with 0·5 per cent. of colouring matter, and when dry it is compared with those patterns which have been previously dyed and have been put in a pattern book. Suppose, for instance, the shade obtained with the new samples compares with the one obtained by dyeing with 0·6 grs. of the standard sample, then the new sample is stronger than the standard in the proportion of 6 : 5, and in working out the proportions, according to the prices, it can easily be seen which is the most advantageous to use.

In printing, the same plan can be followed, that is, to print different patterns with various amounts of colour of the standard sample, and to keep these patterns in a book for future comparison. For example, in the case of a pigment colour, say ultramarine, we might print five patterns, having about the following proportions:—

No. 1.—(*Deepest Shade.*)

20 grs. gum solution (thickening)
25 grs. ultramarine standard
20 grs. egg-albumen

65 grs.

No. 2.

25 grs. gum solution
20 grs. ultramarine
20 grs. egg-albumen

65 grs.

No. 3.

30 grs. gum solution
15 grs. ultramarine
20 grs. egg-albumen

65 grs.

No. 4.

40 grs. gum solution
10 grs. ultramarine
15 grs. egg-albumen

65 grs.

No. 5.

50 grs. gum solution
5 grs. ultramarine
10 grs. egg-albumen

65 grs.

Or the deepest shade can be weakened by adding gum solution in increasing proportions; or a white pigment can be printed at the same time along with the colour in increasing proportion, leaving the amounts of gum and egg-albumen unaltered, while diminishing the amount of ultramarine. For instance, the ultramarine in the five patterns could be taken—25, 20, 15, 10, and 5 grs., and white pigment (preferably sulphate of barium), 5, 10, 15, and 20 grs., beside 20 grs. of gum thickening and 20 grs. of egg-albumen.

In the case of aniline and other colours, the same plan could be followed; in this instance a colour could be prepared, say with methyl violet, with 20 grs. of gum solution (thick), 20 ccs. of methyl violet (5 per cent.) solution, 20 grs. egg-albumen, and the violet solution could be used to produce five patterns in diminishing proportions, in the same way as described for ultramarine, and pigment colours generally.

As explained before, aniline colours could be tested against each other in printing, by the method of fixation with albumen; it is a simple and convenient method, and will be found useful in many cases; however, the method of fixation by means of tannic acid being the one generally employed, it is as well to test colours by printing them by that method.

In the valuation of the aniline dyestuffs by printing them by the tannic acid method, the following plan can be followed:—We have to consider, first, the solution of the colouring matter, then the tanning (fixing) material, the thickening, the necessary amount of acetic acid, and, finally, the strength of the tartar emetic bath which follows after the steaming, as we have already explained.

As a rule it is preferable in the laboratory to dissolve the tannic acid in the gum thickening: for this purpose take

100 grs. gum thickening	1 gal.
10 ,, tannic acid	1 lb.

The gum solution is heated on the water bath or in the double-cased pans heated by steam, and then the tannic acid is dissolved in it, and this solution can be kept as a standard, and will do for several days; or the tannic acid can be dissolved in hot water, and the cold solution kept as standard. If the shades required are not to be of very great brightness, then instead of tannic acid a good sumach extract can be very well used; these extracts come now in the trade in large quantities, and are pretty extensively used by both printers and dyers. It is also necessary to observe in the preparation of the colours, 1st, that the solution of the colouring matter be quite cold before adding to the tannin and gum solution, and, 2nd, that the acetic acid be added before the solution of the dyestuff is added to the tannic acid. If this latter rule is not followed, the colouring matter will combine at once with the tannin, and the lake will be formed before the colour is printed, and therefore not fixed on the fibre, and a poor colour will be the result.

In the case of some colouring matters which are little soluble in cold water—for instance, magenta and safranine—a slightly different plan will have to be followed. In this case the colouring matter can be dissolved in boiling water, either with the addition of methylated spirit or not, and added at once to the hot starch or gum thickening, which is made stronger for the purpose, and the whole is left to cool, when the acetic acid and the tannin solution can be added.

In the case of magenta, it must be observed that some manufacturers sell the same in a very strong solution, and that there is also the acetate of rosaniline in the market, which is much more soluble in water than magenta crystals. In the case of safranine also, there is the safranine paste, which has been employed ever since this dyestuff was first introduced in dyeing and printing, and which can of course be used without any further trouble. The violets also can be bought in ready-made solutions, sometimes also in paste form; and sometimes the blues are sold either in solution or in the form of a paste. In these cases of course no preparation of the dyestuff is necessary, but it can be mixed at once with the other ingredients in the preparation of the colours.

As an example of a tannic acid colour we may take

100 grs. hot gum thickening	1 gal.
10 ,, tannic acid	1lb.

Dissolve, and when cold add

5 grs. acetic acid.	½lb.
10, 20, or 30 grs. cold methyl-violet (2 B.) solution at 5 or 7½ per cent., according to shade required.	1 to 3lbs.

The violet solution is made by dissolving

5 grs. of methyl-violet	½lb.
In 100 ,, of boiling water	1 gal.

Stir until dissolved, leave to cool, and filter.

If a 7½ per cent. solution of violet is required it is advisable to have a little methylated spirit along with the water. For instance, with 7½ to 8 parts of methyl-violet use

20 to 30 parts of alcohol, and
60 ,, 70 ,, of water.

The spirit is added first to the colouring matter, and the whole heated on the water bath, then diluted with the boiling water, which is added in small portions, stirring very often, until all the colouring matter is dissolved.

In dissolving magenta more spirit would have to be used in order to have a strong solution which would keep when cold, but as the cost of the alcohol considerably increases the cost of these colours, it is preferable, when deep shades are required, to dissolve the colouring matters in the boiling water, or even in the boiling thickening, and to add the tannic acid afterwards in solution or in the form of sumach extract. Sometimes in the preparation of these tannic acid colours some tartaric acid is added along with the acetic acid, sometimes also some bisulphite of soda is added, as in the case of methyl-green, both with the purpose of keeping the colours acid, and to prevent the combination of the dyestuff with the tannin before they are applied on the calico, because, as well known, acetic acid is so easily volatile.

In order to give an idea of the corresponding amounts of dyestuff and tannic acid required to produce good shades, we may say that the best results are obtained with about the following proportions :—

For 4 parts of magenta crystals about 5 parts tannic acid.
,, ,, methyl-violets ,, 5 ,, ,,
,, ,, methyl-green ,, 10 ,, ,,

The solution of *tannic acid* can be made by dissolving

100 grs. tannin	10 lbs.
In 100 ,, boiling water	1 gal.

or for weaker colours

75 grs. tannin	7½lbs.
In 100 ,, boiling water	1 gal.

The following recipes can be taken also as an example for preparing a tannic acid colour for printing :—

Violet.

15 grs. methyl-violet are dissolved	1½lbs.
In 200cc. boiling water	2 gals.
And 500cc. gum thickening (1 gum, 1 water)	5 gals. at 10lbs. per gal.

and when cold, add solution made with

140 grs. tannic acid	14lbs.
In 130 ,, boiling water	13lbs.
And 30 ,, acetic acid	3lbs.

Print, dry, steam about one hour, then pass into a tartar emetic bath (double tartrate of potassium and antimony), made by dissolving

2 grs. of the salt	3 to 4 ozs.
in 100 ,, of water	1 gal.

After passing two or three minutes through this bath, it is well washed (and if necessary soaped) and dried. The strength of the antimony bath will vary according to the depth of shade and the amount of colour on the pattern, beginning with a ½ per cent. tartar emetic solution up to 3 per cent. for a heavy pattern, but for ordinary experimental work at 2 per cent. solution of the tartar emetic will be found very useful.

Instead of the latter the cheaper double oxalate of antimony and potash lately introduced in the industry may also be used. For the soaping for small experiments, as a rule, 1 to 2 or 3 per cent. of soap on the weight of the cotton is more than sufficient for the purpose, the temperature of the soap bath being about 40° or 50° C., and the amount of water being about ten times the weight of the cloth to be soaped. The soaping is performed for a few minutes, then the prints are washed and dried.

Methylene Blue.

12	grs. methylene blue	1lb. 3oz.
50	,, acetic acid, 7½° Bé	½ gal.
30	,, wheat starch	3lbs.
100	,, water	1 gal.

are boiled, and when cold, add solution of

	60 grs. tannin	6lbs.
In	60 ,, water	6lbs.

This colour, as in fact all the tannic acid colours, are printed and fixed as above. For lighter shades the standard colours can be reduced by adding more thickening, either gum solution or starch paste. As a general rule it is well to calculate the amount of the colouring matters of the testings in proportion to their prices; but even then, if one should come out stronger than the other, it can be easily ascertained by how much per cent. one is more advantageous than the other, either by further testings, by reducing the stronger colour with 5, 10, or 15 per cent. of thickening, or by comparing the produced shades with the scale of the different depths of shades of printed patterns, obtained by means of different proportions of the standard sample already prepared as before explained.

The malachite or fast greens, or essence of bitter almond greens, can be fixed in the same way, and so can magenta, Bismarck brown and safranine, although the latter, and even sometimes magenta and the violets, are fixed on calico by means of the arsenious acid process, either by arsenious acid dissolved in glycerine, or by the arsenite of soda along with acetate of alumina, the colours being developed by steaming. The shades thus obtained are faster and much brighter than those obtained by means of tannic acid; and this applies especially to the aniline blues in paste form, such as cerulean or gentiana blue, etc., which give remarkably bright and pretty fast shades against boiling soap, which shades, however, unfortunately, do not stand light well.

For methyl-green a slightly different plan is followed in the method of printing. Either bisulphite of soda is used along with the other ingredients in the preparation of the colours, taking about the same quantity of bisulphite of soda at 50° Tw. that is taken of acetic acid, or acetate of chrome or alumina are used along with the tannin and the acetic acid, etc., as shown in the following example:—

Methyl-Green.

10 grs.	tannic acid dissolved	1lb.
200 ,,	acetic acid 9° Tw. at about 45° to 50° C.	2 gals;
then add		
270 ,,	sumach extract at 22 Tw.	$2\frac{3}{4}$,,
and boil with		
90 grs.	starch previously mixed	9lbs.
with		
150 ,,	water	$1\frac{1}{2}$ gals.;
then add		
50 ,,	tartaric acid	5lbs.
20 ,,	acetate of chrome at 22° Tw.	2lbs.
When cold add a solution of		
30 grs.	methyl-green	3lbs.
In 110 ,,	water	$1\frac{1}{4}$ gals.

print, steam, pass through tartar emetic solution at about 65° C., wash, etc.

As will be easily understood, compound colours can be formed on the fibre by printing two or more of the aniline dyestuffs, which are fixed by means of the tannic process;

and, in fact, this is done in practice, especially for the production of deep blue shades, by taking, for instance, methylene blue and methyl violet in different proportions, according to the shade required. Violets and greens also produce deep blue colours on calico, and are extensively used for the purpose in printworks, but the shades obtained are not as bright as those produced by means of methylene blue and violet. It is useless to say that the printing process is just the same in the fixing of these compound shades as it is in the fixation of the single colours themselves. The dyestuffs are, as a rule, dissolved separately, and the solutions kept as standards, and then added when mixing the colours, in proportion to the shade required, or else the colouring matters can be weighed out and dissolved at the same time, if it is known the amount of the dry powders required to produce a certain shade.

In commerce there are in fact definite mixtures of, say, methylene blue and violet or green and violet, which are sold sometimes under assumed names, and which are carefully prepared by the colour manufacturers to produce definite shades. We have mentioned before that some of the basic aniline colours—such as magenta, violets, and especially the aniline blues in paste form, are sometimes printed by the means of arsenite of alumina; by this means brighter shades are obtained, which stand pretty well even boiling soap. A colour can be prepared as follows :—

Aniline Blue Paste.

100 grs. acetate of alumina, 15° to 20° Tw.	1 gal.
10 grs. starch	1lb.

Boil, and when cool, add

20 grs. arsenic and glycerine standard	2lbs.
10 or 15 grs. of blue, in paste form	1 to 1½lbs.

The arsenic and glycerine standard is made by dissolving

50 grs. white arsenic (arsenious acid)	5lbs.
In 100 grs. glycerine at 28° Bé	1 gal.

The operation of dissolving the arsenious acid in glycerine is performed on the water bath, or in a double cased pan heated by steam, by constant stirring until all is dissolved. After printing and drying, the goods are steamed at 4lbs. pressure (or more) and soaped. Instead of the blue in paste form, other colours can be employed, either in paste or solution, for instance, the methyl violets, indulines etc.

The arsenic and glycerine standard can be made also weaker; but the above proportions will do for a full blue, and the colour can be easily diluted with thickening for obtaining lighter shades. The arsenic method is not so much used now for the other colours as the tannic acid process, but for the blue, the arsenious acid fixation gives a much brighter shade than is obtained by the other method, and on this account it is preferred. In Germany the employment of arsenious acid for the fixation of colours is forbidden by law, and the attempt was made some years ago to do the same in England, but the project fell through.

The employment of arsenious acid, in this case, is not so objectionable as it might seem, provided, however, that the goods when steamed are thoroughly well soaped and washed, since the small amount of arsenic present will be then in the form of insoluble arsenite of alumina, and will not act injuriously.

The acid colours are not so much employed in calico printing as the aniline basic dyestuffs; the aniline blues, however, are pretty largely used, and they supply shades which will stand even a lukewarm soaping, and are also very bright, but they do not come up in point of fastness to the insoluble aniline blue in paste form, neither do they produce such bright shades. Alkaline blue could be used from the same recipe as the above, that is, with arsenic and glycerine and acetate of alumina; the colour being previously dissolved in boiling water, and kept in solution for use. Or the following recipe can be employed with advantage:

Alkaline Blue.

1,000 grs. water	1 gal.
150 grs. starch	1½lbs.

Boil, then add solution of

50 grs. alkaline blue	½lb.

Stir till cold; then add

125 grs. bisulphite of soda, 35° Bé	1¼lbs.
90 grs. acetate of chrome, 15° Bé	15ozs.
10 grs. olive oil	2ozs.

Print, dry, steam for one hour, and soap at about 40° C. It can also be printed by a modification of the tannic acid process along with bisulphite of soda.

The ordinary soluble blues, that is the bi and trisulpho compounds of phenylated rosaniline, are also used in printing; but only in cases where no fastness is at all required, and sometimes they are printed simply thickened with starch paste, but for fixing them generally, red liquor or acetate of alumina is employed, with or without bisulphite of soda. The following recipe may be taken as an example:

Aniline Blue Soluble in Water.

100 water	1 gal.
10 starch	1lb.

Boil, and while still hot, add

5 grs. of aniline blue	½lb.

Stir, until cold, then add

20 grs. bisulphite of soda, 35° Bé	2lbs.
15 grs. acetate of alumina, 15° Bé	1½lbs.

Print, steam, and wash slightly. Better results are obtained if the cloth has been previously prepared with a 5 per cent. solution of oleine. Of the remaining acid dyestuffs, we have the eosines and the azo products, especially the azo scarlets. The azo scarlets give very bright shades, and are employed to a pretty large extent; but they are, unfortunately, very loose against soap, although they stand light fairly well, Many attempts have been made to fix the scarlets permanently on cotton, both by dyeing and printing, but they have all failed so far, and will always fail when it is a question of the employment of sulphonic acid colours; but it would be different if the azo scarlets could be applied on the fibre as basic colouring matters. This is done, in fact, in dyeing where fast scarlets are fixed on cotton yarn or cloth by Holliday's method, and the same principle has been tried in printing, but not up to the present with marked success. The eosines are sparingly employed in printing, owing to their fugitiveness against light. There are several methods of fixation relying either on the employment of alumina mordants or arsenite of alumina, or even tannic acid, the latter colour being printed on cloth prepared with glue or gelatine, the former on calico prepared with stannate of soda.

But by whichever method the eosines are fixed they will not stand soaping, and soon fade when exposed to light, and therefore the eosines had better not be largely employed in calico printing, since it is scarcely of any utility to print colours which fade appreciably after only a few hours' exposure.

The azo scarlets can be printed by the following methods:

Azo Scarlet.

10 grs. azo red	1lb.
12 grs. starch	1¼lbs.
100 grs. water	1 gal.
15 grs. aluminate of soda 15° Bé	1½lbs.
2 grs. olive oil	3oz.

Boil, cool, print on cloth preferably prepared with oleine or stannate of soda. The colour is developed by steaming in the usual way.

Acetate of alumina or acetate of chrome can be employed for the fixation, but in the case of the chrome mordant the red is not so brilliant. A recipe similar to the one for soluble aniline blues can also be followed for the fixation of scarlet, only the bisulphite of soda is eliminated, as for example,

Azo Scarlet.

100 grs. water	1 gal.
12½ grs. starch	1¼lbs.

Boil, and while still hot, add

10 grs. azo scarlet	1lb.

Stir until cold, then add

30 grs. acetate of alumina 20° Bé	3lbs.

Print on cloth prepared with oleine, and steam.

For the fixation of a fast azo red (not sulphonic product, but the basic dyestuff) the following process, by Graessler, can be employed:—

Naphtol Red.

100 grs. water	1 gal.
9 grs. starch	14oz.
5 grs. b. naphtol	8oz.
4·8 grs. xylidine	7oz.
2·8 grs. nitrite of sodium	3¾oz.
4 grs. sal ammoniac	7oz.

steaming being necessary for the development of the colour, but the red obtained by this method cannot be compared to the one produced by alizarin, either in point of fastness or brilliancy of shade.

Of the other acid azo colouring matters the oranges are employed to a very moderate extent in calico printing, and so are the other products of a similar nature, they being mostly used in silicious printing (for linings) the colour being simply mechanically fixed on the fibre by means of starch paste.

Before leaving this class of colouring matters we must also mention coralline, one of the earliest of the coal tar colours introduced into practice and a derivative of carbolic acid.

It is not so much employed now as formerly, but it still finds employment in calico printing and in paper staining.

Red Coralline.

100 grs. water	1 gal.
15 grs. starch	1¼lbs.
Boil, and when still hot add solution of	
12 grs. red coralline	1¼lbs.
In	
40 grs. water	4lbs.
And	
10 grs. glycerine	1lb.
And when all is cold add	
20 grs. of magnesia	2lbs.
Previously mixed with	
40 cc. cold water	4lbs.

Print, steam, and wash.

Another recipe for obtaining a yellower shade is the following:—

Red Coralline.

A lake is first formed by precipitation, the coralline is dissolved in caustic soda, and the lake precipitated out by means of tin chloride solution.

12 grs. of dry coralline

are dissolved in

4 grs. of caustic soda lye at 30° Bé., and
60 cc. water,

and when the solution is complete it is made up with cold water to 1 litre, filtered, and precipitated by means of tin salt solution until no more precipitate is formed; it is then filtered and drained on filter until a pretty stiff paste is formed. This coralline paste is mixed with

80 grs. starch paste at 10 per cent.
1 gr. magnesia.
2½ grs. oxalic acid.

Coralline colours give better results on cloth previously prepared with alumina. In the preparation of steam colours, which are fixed by means of acetate of alumina, two ways can be followed; the alumina mordant can either be added to the thickened colour or a weaker acetate of alumina can be employed instead of the water in the preparation of the starch paste, as shown in the recipe for aniline blue in paste form. As a rule an acetate of alumina of about 10° Tw. will be sufficient for general work, but for deeper shades of course a stronger acetate of alumina must be employed. It is also to be observed that in many cases starch paste has been given as the thickening material to be employed; for ordinary work starch paste is the most convenient of the different thickenings when printing with a small roller printing machine; for block printing, as already mentioned, gum solution is much to be preferred. In working with the block the recipes where the starch paste is used will have to be modified slightly.

ALIZARIN.

We now come to the most important dyestuff for calico printing, viz., alizarin, which is fixed on calico by two distinct methods, either by dyeing or by printing; in the latter case steaming being necessary for the development of the shades. We will now mention the second method (the steaming method), generally known as the extract style, while the methods of producing the different shades with alizarin by dyeing, or by the so-called madder style, will be treated afterwards separately. It is well known that the extract style, although preferable to the other for the greater simplicity of manipulations, and for the advantage of being able to connect alizarin red and other alizarin shades with the great variety of steam colours now existing, does not produce such bright reds as those obtained by the dyeing methods. The shades generally produced with alizarin in printing, by the steaming process, are reds, pinks, purples, chocolates, and browns of great variety; in some cases very bright shades, and in all cases absolute fastness. As a rule the majority of these alizarin steam colours are printed on cloth previously prepared with oleine or alizarin oil. The cloth being passed for the purpose through a 5 or 10 per cent. solution of oleine, and dried on the cylinder;

by this means, especially in the case of the reds, brighter effects are produced. Alizarin now comes in the market principally as a 20 per cent. paste, and therefore on all the following recipes this standard will be followed.

In alizarin works, and very often also in printworks, alizarin is tested by the dyeing methods in two ways: either plain cloth, previously mordanted with alumina, or oleine and alumina, is dyed in alizarin, and brightened, steamed, and soaped in the usual way, as for alizarin dyeing, as will be mentioned later on when speaking of the methods for producing discharged patterns on turkey red and alizarin red dyed goods. Alumina and iron mordants, or mixtures of both, are printed in stripes, aged, dunged, dyed, etc., as will be described later on.

The colours obtained by the steam methods with alizarin are:—reds and pinks with alumina mordants, purples with iron, and chocolates with mixtures of iron and alumina mordants. A very fine chocolate brown is also obtained by the employment of chromium mordants. As a general rule the acetate of alumina is employed for reds and pinks, either alone or in conjunction with a small amount of tin or of nitrate of alumina; while for purples, acetate of iron or the cheaper pyrolignite of iron is used; the acetate of chrome has come more and more prominently into use, not only in connection with alizarin, but with many other dyestuffs, as we shall see in describing the other steam colours.

In the printing of steam alizarin reds, great difficulty was at first experienced in obtaining good reds, on account of the colour reacting, when printing, on the steel doctors of the calico printing machines, but it was found afterwards that a small addition of sulphocyanide of ammonia or potassium prevented the injurious action of the iron, which soon impairs the beauty of alizarin reds by imparting a dull bricky appearance to them.

In the last few years the sulphocyanide of alumina itself has been employed instead of the acetate for producing steam reds with alizarin.

STEAM ALIZARIN COLOURS.

Red, with Acetate of Alumina.—No. 1.

100cc. water	1 gal.
50 grs. acetic acid 8° Tw	½ gal.
35 to 40 grs. alizarin, 20 per cent	3½lbs.
10 grs. olive oil	1lb.
10 grs. acetate of lime 14° Tw	1lb.
15 grs. starch	1½lbs.

boil, stir until cold, then add

10 grs. acetate of alumina 20° Tw	1lb.

mix, print, dry, and steam.

Red.—No. 2.

100 grs. starch paste	1 gal.
35 grs. alizarin, 20 per cent	3½lbs.
5 grs. nitrate of alumina, 20° Tw	½lb.
7½ grs. acetate of alumina, 20° Tw	¾lb.
5 grs. acetate of lime, 20° Tw	¼lb.

This recipe will give a deeper red than the above, and if a lighter shade is required the amount of thickening can be increased.

Red.—No. 3.

170 grs. water	3½ gal.
40 grs. starch	8lbs.
40 grs. tragacanth solution	8lbs.

boil, and when cold, add

35 grs. olive oil	7lbs.

previously mixed with

15 grs. chloride of lime solution, 12° Tw	3½lbs.

then add further

75 grs. alizarin 20 per cent	15lbs.
100 grs. sulphocyanide of alumina, 10° Tw	20lbs.
10 grs. tin solution, as below	2lbs.
5 grs. acetate of lime 20° Tw	1lb.

Tin Solution for No. 3 Red.

Acetate of tin, 20° Tw.*

In

100 grs. water	1 gal.

dissolve

75 grs. tin crystals	7½lbs.
100 grs. acetate of lead	10lbs.

leave to settle, filter, and make up to 20° Tw. with cold water.

Brighter reds are now obtained by means of the sulphocyanide of alumina than those produced by means of the acetates or nitrates; this is due to the fact that the sulphocyanide prevents the injurious action of the iron, dissolved by the colours from the steel doctors of the printing machines. The smallest amount of iron spoils the beauty of alizarin reds either in dyeing or printing, and to get over the difficulty of having the reds dulled by the even minute quantity of iron taken up from the steel doctors during the printing of the pieces, the sulphocyanide of ammonia was pretty largely used some years ago; a small amount being generally added to the printing of alizarin red colours. The sulphocyanide of alumina has further the advantage that, unlike the acetates, it is not decomposed except when steamed, and fuller and more even colours are the result.

As remarked when mentioning the fixing of aniline colours for laboratory work an acetate of alumina paste, prepared by boiling

10grs. starch

in

100cc. of acetate of alumina at about 8° Tw.

will be found very useful, as also for the testing of alizarin colours.

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* It has already been mentioned, in the chapter relating to Mordants, page 125, that, owing to the method of preparation, acetate of tin is not often employed on account of the lead it contains. Instead of the acetate the other tin preparations, such as the oxalate, citrate, or sulphocyanide of tin could be used with more advantage, for which see page 124, where their preparations are indicated.

The latter is used in proportion according to the shade required; a good printing colour for laboratory experiment can be prepared as follows:—

100grs. acetate of alumina paste as above,
15 to 20 grs. alizarin, 20 per cent.
10cc. acetic acid 10° Tw.
1grs. sulphocyanide of ammonia,
5gr. olive oil.

The last two could be even left out, but brighter colours are produced by their means.

The alizarin red colours are printed on calico, which has been previously oiled with oleine, 5 or 10 per cent. solution, and dried. After printing it is steamed for one hour or one hour and a half. If a steam chest is at hand it can be steamed with or without pressure, if no steam is at hand then a very simple method can be employed; a large flask is used, heated on a "Bunsen" burner, in which the water is maintained at a good boil, so that it will produce a large amount of steam; the pattern to be steamed is wrapped in flannel and introduced into the neck of the flask and kept there, and prevented from falling either by means of a string or by means of a wire. At the top of the flask one or two rings of flannel are applied, which are kept down by a slight weight, to assert in a certain way a gentle pressure. Good results have sometimes also been obtained by the employment of a so-called potato steamer, which consists of a common kitchen saucepan, on which is fixed a tin cylinder provided with a cover, and having a perforated bottom through which the steam is compelled to pass. Although it is by many believed that the higher the pressure the better the reds, this is not always the case, especially with dyed alizarin reds, as I have seen some good colours obtained even in a common steamer, as just mentioned, where, of course, no pressure can be obtained. In using this a precaution must be taken, and that is, that the printed patterns must be wrapped in flannel several times, or else they easily get wet, and the colour is not even developed. The saucepan itself must be placed either on a good fire or on a good gas lamp, so that it will produce a large quantity of steam; the tin cylinder must be well covered several times with wool or flannel, in order to prevent loss of heat by radiation.

Steam reds by means of the acetates are more readily obtained by steaming as described, than those prepared with sulphocyanides; these require a hotter steaming, and consequently they are very seldom obtained in the laboratory unless there is a boiler at hand, and a proper steam chest.

After steaming, the patterns must be passed through a chalk bath at about 45 to 60° C., containing

1 litre water	10 gals.
30 grs. chalk	3lbs.
1½ grs. tin crystals	2½oz.

where they are worked for five or six minutes and then washed, and afterwards soaped.

In the laboratory, as a rule, the soapings as performed in a boiling soap bath, containing about five parts of soap to every 100 parts of cloth, but by this means the reds are very often, if not spoilt, at all events considerably weakened.

It is better to soap the patterns in a systematic way, by using two or three baths at increased temperature, as for instance:—For 100 grs. calico—

First Soap Bath.

2 grs. soap.

previously dissolved in boiling water, and added to bath, which is made up to about 54° C. Patterns are worked in this bath only a short time, not more than 10 minutes or a quarter of an hour, then washed.

Second Soap Bath.

3 grs. soap,
¼ ,, tin crystals.
Temperature, 60° C.

duration, 20 minutes, then washed.

Third Soap Bath.

4 grs. soap.
½ ,, tin crystals.
Temperature, 70 to 75° C.

duration, 20 to 30 minutes, then washed and dried.

It is a well-known fact that tin asserts a very beneficial effect in the production of alizarin reds, which are always obtained brighter by its means, and of a yellower shade; it is also to be observed that goods which have been either prepared in oleine before printing, or oiled after, will produce better reds if they are exposed to air for some time before they are soaped. The quality of soap is also of great importance, since, if it is alkaline it will impoverish the shades. By diluting the alizarin printing colours, rose or pinks are produced.

This is simply done by adding more starch paste to the colours, as described above.

Sulphocyanide of alumina yields brighter pinks than the acetate.

In printworks the practice of steaming varies considerably. While aniline colours generally are steamed, sometimes at about 4lbs. pressure, alizarin steam reds are sometimes steamed at much higher pressure, some printers maintaining that at much higher pressure better colours are the result. The brands of alizarins generally used for steam reds are those of yellow shades, because they give a colour which is more pleasing to the eye, as can be easily understood; if required, however, blue shades of alizarin can be employed, the methods being just the same. For purples the blue shade is mostly employed.

Alizarin Purple.

100 grs. starch thickening	1 gal.
20 grs. alizarin, blue shade	2lbs.
15 grs. acetic acid 8° Tw	1½lbs.
10 grs. acetate of lime, 20° Tw	1lb.
20 grs. acetate of iron, 20° Tw	2lbs.

The shade produced is rather dark, but if a lighter purple is required, the colour is, of course, reduced by means of starch thickening. When printed, the cloth is steamed at 7 or 8lbs. pressure for one hour, then passed through a chalk bath, as was mentioned for alizarin steam red, and then soaped in two or three soap baths, with about 2 to 5 per cent. soap in each.

Brighter shades are obtained by printing on cloth prepared with oleine, and especially by adding to the above colour a small amount of methyl violet solution, arsenic, and glycerine.

To the above recipe could be added,

1 gr. methyl violet	1½oz.
dissolved in	
22 cc. water	2lbs.
and further	
5 grs. arsenic and glycerine solution	½lb.

Alizarin Chocolate.

This is generally produced by a mixture of the alumina and iron mordants, the shade varying, of course, according that more or less iron or alumina has been put into the colours; they are also printed and fixed just in the same way as the two preceding colours. In printworks, as a rule, the residues of the alizarin red colours are employed for the production of these chocolates, being mixed with the necessary amount of iron, acetate, or red prussiate, or even chrome acetate, to produce the shade required.

For laboratory experiment the following can be tried; the proportion of iron and alumina acetate can be modified by taking more or less of each.

100 grs. starch thickening.
20 grs. alizarin, 20 per cent.
15 grs. acetic acid.
10 grs. acetate of lime, 20° Tw.
10 grs. acetate of alumina, 20° Tw.
10 grs. acetate of iron, 20° Tw.

Alizarin Brown (Puce).—No. 1.

100grs. starch thickening 12 per cent.	1 gal.
25grs. alizarin 20 per cent.	2½lbs.
25grs. acetate of chrome, 25° Tw.	2¼lbs.

Alizarin Brown.—No. 2.

100grs. starch thickening 12 per cent.	1 gal.
30grs. alizarin 20 per cent. blue shade	3lbs.
30grs. nitro-acetate of chrome, 45° Tw.	3lbs.
3grs. acetate of lime, 20° Tw.	5ozs.

Of the other alizarin colours, the orange and the blue must be mentioned. Although not largely used they will still be found useful in special cases.

Alizarin Orange.

100grs. starch thickening	1 gal.
30grs. alizarin orange	3lbs.
15grs. nitrate of alumina 20° Tw.	1½lbs.

Alizarin Blue—No. 1.

In

100grs. hot starch thickening 12 per cent.	1 gal.

dissolve

5grs. alizarin blue S	½lb.

when cold add

30 grs. acetate of chrome, 15° Tw.	3lbs.

Alizarin Blue.—No. 2.

100grs. thickening 14 per cent.	1 gal.
50grs. alizarin blue paste 10 per cent.	½ ,,
20grs. acetate of chrome, 20° Tw.	2lbs.
30grs. nitrate of magnesia, 20° Tw.	3lbs.

There are other colouring matters which are classed with the alizarin colours, although they do not belong in reality to them, as, for instance, galleine and ceruleine, etc., which, however, yields shades which come very near to alizarin in point of fastness, and which are employed by the same methods of fixation, principally by means of acetate of chrome, a product which, as remarked before, has been found of such utility in the last few years in calico printing.

Very nice shades are obtained by means of ceruleine, which has been somewhat largely employed in the last few years, either as self colour or in connection with other dyestuffs. It is sold either in the form of a paste or in combination with bisulphite of soda, as a powder soluble in water, under the mark ceruleine S, in the same way as alizarin blue.

Ceruleine Olive.

100 grs.	starch thickening	1 gal.
35 grs.	ceruleine paste, 10 per cent.	3½lbs.
10 grs.	bisulphite of soda, 50° Tw.	1lb.
10 grs.	acetate of chrome, 40° Tw.	1lb.

The ceruleine paste and bisulphite are first mixed and allowed to stand two or three hours before adding the acetate of chrome; finally the thickening is added and the colour printed; the cloth is then steamed for an hour and a half to two hours at a pressure of about 5lbs., then passed through a chalk bath, at about 70° C., containing 10 per cent. whiting, washed and soaped.

Galleine Violet.

100 grs.	thickening	1 gal.
10 grs.	acetate of chrome, 40° Tw.	1 gal.
15 grs.	galleine paste, 10 per cent.	1¼lbs.

Print as soon as possible, after mixing, on cloth prepared with oleine, and steam in the usual way, when a nice violet is produced. In all the processes previously described we have given the amount of the materials, as far as possible, in simple proportions, but it will be readily understood that either the thickenings or proportions of the ingredients can be modified according to requirement—for instance, the following recipe for ceruleine printing may be taken as illustration.

Ceruleine Olive.

60 grs. ceruleine paste	2lbs.
30 grs. bisulphite of soda, 30° Tw	1lb.

mix, leave to stand three hours, then add

300 grs. thickening	1 gal.
12 grs. acetate of chrome, 30° Tw	1lb.

Thickening for Ditto.

8 grs. starch	1lb.
8 grs. dextrin	1lb.
40 grs. tragacanth water	½gal.
80 grs. water	1 gal.
20 grs. olive oil	2½lbs.

Of the other artificial colouring matters, belonging to this class, may be mentioned anthragallol and gallocyanine, the first of which is fixed by similar methods to those of alizarin, and yields similar shades, and the gallocyanine yields violet-blue shades when printed with acetate of chrome, and by the addition of Persian berry extract, can be made to yield colours very close to indigo blues. The following recipe has been found to give good results in practice :—

After printing, steam in the usual way.

Gallocyanine Violet.

100 grs. gallocyanine paste	1 gal.
75 grs. tragacanth mucilage	¾ gal.
25 grs. acetic acid, 9° Tw	¼ gal.
25 grs. alizarin oil	¼ gal.
15 grs. starch	1½lbs.

Boil, stir until cold, and add

12½ grs. acetate of chrome, 40° Tw.	1¼lbs.
6 grs. yellow prussiate	½lb.

Before concluding the review of the methods of fixation of the artificial colouring matters by the steaming processes, it is necessary to mention a product lately introduced, a bisulphite of sodium derivative of an azo red, under the name of azarine S; it yields shades brighter than alizarin for reds and pinks, but not quite so fast.

Azarine Red.

100 grs. starch thickening, 15 per cent.	1 gal.
5 grs. acetic acid, 8° Tw.	½lb.
12 to 15 grs. azarine S. paste, 20 per cent.	1 to 1½lbs.
10 grs. acetate of aluminium, 20° Tw.	1lb.

The colour is developed by steaming for one hour, in the usual way.

DYEWOOD EXTRACT COLOURS.

This is an important class of colouring matters, which are even now very largely used in printing; in fact, from these the "steam" or extract style derives its name. Formerly it was the rule in all large works to prepare their own extracts, while now there are few printworks where they are prepared, as the industry of dyewood extract has been largely developed in the last 15 or 20 years, and very good products are found in commerce. The most important of the dyewood extracts in calico printing is still the logwood extract, which is employed in very large quantities for the production of steam blacks, and in a smaller way in the production of compound shades. In spite of the competition of the aniline black, logwood still holds its own in printing, because it can be applied for a great many purposes for which aniline black cannot be employed.

The best logwood steam blacks are produced by means of chromium mordants, principally acetate, nitro-acetate, and lately sulpho-cyanide of chrome; and, as a rule, a small amount of chlorate, either of sodium or potassium, is added to the colours, which is very useful to the fixation of the black lake by the oxidising action it asserts. There is a very great variety of recipes for logwood steam blacks, from which the following are selected:

Steam Logwood Black.—No. 1.

100 grs. water	1 gal.
100 grs. acetic acid, 6° Tw.	1 gal.
100 grs. logwood extract, 30° Tw.	1 gal.
20 grs. quercitron extract, 30° Tw.	2lbs.
50 grs. starch	5lbs.
25 grs. dextrin	2½lbs.
5 grs. olive oil	½lb.
7 grs. chlorate of potash or soda	¾lb.

boil, stir, until cold, then add

100 grs. acetate of chrome, 20° Tw.	1 gal.

In some cases a small amount of glycerine or turpentine is added to the colour.

The quercitron or bark extract, for which sometimes Persian berry extract is employed, is used in order to form a jet black, by the yellow tone it gives, without which a blue black is produced, which, if diluted with more or less thickening will give deep indigo-like shades, and if very dilute, greys of different strength. Instead of the chlorate of soda or potash, the corresponding amount of the chlorate of aluminium solution may be employed, when a finer black will be produced.

Steam Logwood Black.—No. 2.

150 grs. water	1½ gal.
100 grs. acetic acid, 6° Tw.	1 gal.
125 grs. logwood extract, 30° Tw.	1¼ gal.
50 grs. starch	5lbs.
25 grs. dextrin	2½lbs.
5 grs. olive oil	½lb.
8 grs. chlorate of potash or soda	¾lb.

Boil, stir until cold, then add

30 grs. nitro acetate of chrome, 34° Tw	3lbs.
5 grs, yellow prussiate, in fine powder	¼lb.

Stir until all are dissolved, then print and steam.

There are now some logwood preparations in commerce, which yield very good steam blacks. They are sold under different names, and as a rule makers give the methods of their employment. Generally they are simply mixed with thickening, acetate of chrome and acetic acid, to give a colour, which, when printed and steamed yields a very good black. For instance ;—

Steam Black.—No. 3.

40 to 50 grs. steam black (commercial paste)...	½ gal.
100 grs. starch paste, 15 per cent.	1 gal.
20 grs. acetic acid, 10° Tw......	2lbs.
5 grs. acetate of chrome, 30° Tw.	½lb.

These preparations vary in strength, consequently the amount of the commercial preparation must be calculated accordingly, the above recipe referring to one of medium strength.

The iron steam blacks are not so much employed now as they were formerly, as those produced by chrome are preferred. The following recipe may, however, be taken as an illustration :—

Steam Logwood Black.—No. 4.

60 grs. starch	6lbs.
60 grs. flour..	6lbs.
250 grs. acetic acid, 6° Tw.	2½ gals.
350 grs. logwood extract, 20° Tw.	3½ gals.
350 grs. acetate of iron, 15° Tw.	3½ gals.
15 grs. olive oil	1½lb.

Are boiled, stirred until cold, then printed and steamed in the usual way.

These iron blacks can be greatly modified by the addition of other mordants to the iron acetate ; for instance, by the joint employment of acetate of aluminium, and also by the use of copper salts. It can also be modified by employing either extract of galls or sumach, along with the logwood extract.

Logwood gives different colours with different mordants, for instance, it gives a violet or purple with alumina, but except for blacks and deep blues it is now seldom used by itself for the production of other shades. It is, however, largely employed in the production of compound shades such as browns, chocolates, etc., as will be seen later on.

For the production of steam blacks, except logwood, and to a certain extent galls and catechu, which are sometimes employed along with logwood, there is no other dyestuff which is used in printing. There is, of course, the aniline black, but this cannot be called in reality a steam colour; and no aniline black would stand steaming under a heavy pressure, therefore it will be classed with the oxidation colours, and mentioned later on.

Logwood Purple.

100 grs. logwood liquor, 15° Tw.	1 gal.
100 grs. acetate of alumina, 20° Tw.	1 gal.
2½ grs. soda crystals	4 oz.
5 grs. red prussiate	8 oz.
5 grs. oxalic acid	8 oz.
20 grs. starch	2lb.

Boil, stir until cold, and the colour after straining is ready for printing and steaming in the usual way. There are several logwood preparations in the market sold under different names, such as indigo substitute or steam indigo blue, which are printed by means of acetate of chrome in the same way as the commercial steam blacks, but in some cases require the addition of bisulphite of soda to the printing colour.

RED WOODS.

Since the introduction of aniline colours and of alizarin the red woods have lost a great deal of their importance, and are now not often used as self colours, but they are still used to a great extent in compound shades, principally for the production of chocolates, browns, etc. The red woods go under different names in commerce, according to the locality from which they are obtained, but in the print-works their extracts are principally employed, among which

Sapan extract is perhaps the most extensively used. With alumina, reds are obtained which are modified in tone by the addition of bark or quercitron extract to give yellow shades, as for example :—

Sapan Wood Red.

100 grs.	Sapan liquor, 10° Tw.	1 gal.
25 grs.	bark or quercitron extract, 10° Tw.	2½lbs.
15 grs.	starch	1½lbs.

Boil, and while still hot add

1 gr.	chlorate of soda	1½oz.

when cold, add

30 grs.	acetate of alumina, 20° Tw.	3lbs.

Pinks are sometimes produced by means of these red wood extracts, either alone or in connection with cochineal, as for instance :—

Sapan Wood Pink.

100 grs.	Sapan liquor, 4° Tw.	1 gal.
4 grs.	sal ammoniac	½lb.
10 grs.	pink salt	1lb.
½ gr.	oxalic acid	¾oz.
½ gr.	sulphate of cooper	¾oz.

Mix well until all are dissolved, then add

100 grs.	thickening, either strong gum or starch thickening, at 15 per cent.	

Although not belonging to the class of dyewoods, cochineal may still be mentioned here. It has lost much of its importance, especially since the introduction of azo scarlets.

Cochineal Red.

100 grs.	cochineal liquor, 10° Tw	1 gal.
5 grs.	bark liquor, 30° Tw.	½lb,
10 grs.	starch	1lb.
2½ grs.	binoxalate of soda	¼lb.

Boil, stir until cold, then add

5 grs.	of tin solution prepared as below	½lb.

Print, dry, steam gently, and wash.

TIN SOLUTION.

Dissolve

50 grs. tin crystals	5lbs.
75 grs. crystallised stannic chloride	7½lbs.

in

75 grs. hot water	¾ gal.

Dissolve separately

15 grs. acetate of lead	1½lbs.

in

30 grs. boiling water	3lbs.

Add both hot solutions together, stir, leave to settle, filter and use clear liquor.

Cochineal Pink.

100 grs. cochineal liquor, 6° Tw.	1 gal.
5 grs. white tartar	½lb.
5 grs. alum	½lb.
1 gr. oxalic acid	1½oz.
100 grs. gum or other thickening	1 gal.

This pink, without the thickening, can be used for the production of light compound shades of great variety, as lilacs, etc.

Cochineal Rose

is similar to the above, only acetate of alumina is used instead of the alum.

100 grs. concentrated cochineal liquor	1 gal.

obtained from

15 grs. cochineal	1½ lbs.

are mixed with

25 grs. acetate of alumina, 15° Tw.	2½lbs.

and

2½ grs. oxalic acid	¼lb.

And diluted with its own weight or volume of thickening, or even more, according to shade required.

Of the extract yellows, only quercitron and principally the Persian berry are used.

Quercitron or Bark Extract Yellow.

100 grs. quercitron extract, 15° Tw.	1 gal.
50 grs. nitrate of alumina	½ gal.
25 grs. starch	2½lbs.
50 grs. water	½ gal.

Boil, stir until cold, print, steam, etc., or in the same manner as already stated of acetate of alumina, starch thickening is prepared, and mixed with the necessary amount of bark extract along with acetic acid.

Bark extract gives also good yellows with acetate of chrome, but of different hue than the one obtained with alumina, and the chromium mordant is especially useful when the yellow is wanted, not as a self colour, but for the production of olives in connection with logwood or logwood preparations.

Flavine, which is a purer derivative from bark than the ordinary extract, is also used for the production of yellows, as for instance:

Flavine Yellow.

100 grs. water	1 gal.
12½ grs. starch	1¼lb.
10 grs. acetic acid	1lb.
5 grs. flavine	½lb.

are boiled, and when cold add

7½ grs. tin crystals	¾lb.

dissolved in

15 grs. water	1½lb.

and

15 grs. acetate of lime, 20° Bê	1½lb.

The yellows obtained by means of Persian berries are, however, even more largely employed than those produced by means of the bark extracts.

PERSIAN BERRY YELLOW.—*No.* 1.

100 grs. Persian berry extract, 15° Tw.	1 gal.
50 grs. acetate of alumina, 20° Tw.	½ gal.
20 grs. starch	2lbs.
10 grs. tragacanth mucilage	1lb.
5 grs. acetate of lead	½lb.
50 grs. water	½ gal.

boil, stir until cold, then add

5 grs. tin crystals	½lb.
5 grs. acetate of lime, 20° Tw.	½lb.

Persian Berry Yellow.—No. 2.

100 grs. berry extract, 10° Tw.	1 gal.
12 grs. starch	1½lb.

Boil, then add

10 grs. citrate of tin	1lb.
10 grs. acetic acid, 10° Tw.	1lb.
10 grs. acetate of lime, 24° Tw.	1lb.
2 grs. acetate of soda	4oz.

In some cases acetate of chrome is employed along with the citrate of tin, but as a rule the chromium mordant is employed when the yellow is used for the production of olives by means of logwood or logwood preparations. The citrate of tin is obtained by treating tin crystals with citrate of soda.

Citrate of Tin.

50 grs. citrate of soda, 30° Tw	1 gal.
20 grs. tin crystals	4lbs.
20 grs. water	½ gal.

Mix well before use.

Citrate of Soda, 35° Tw., for the above.

20 grs. citric acid crystals	4lbs.

are dissolved in

25 grs. boiling water	½ gal.

then neutralised with about

50 grs. caustic soda lye, at 45° Tw.	1 gal.

The whole is then made up to 35° Tw.

CATECHU.

This material is very largely employed in printing for the production of fast browns of great variety, according as they are mixed or not with other dyewood extracts or colouring matters. The catechu colours can be divided into two classes, those which require chroming or passage through bichromate of potash, in order to develop the browns, and those which are fixed in a direct way, the shade being developed by the steaming process and consequently not requiring the passage through chrome. The colours requiring chroming for their development can only be connected in printing with those shades which stand the same treatment, for instance, in goods printed with logwood or even aniline blacks, yellow produced by printed lead salts requiring to be developed or raised by a chrome bath, etc., and for this reason can only find a limited employment, while steam catechu colours can be connected with all the other shades fixed by steaming, and are found therefore more generally useful.

Steam Catechu Brown.—No. 1.

In	
100 grs. catechu solution, 20° Tw.	1 gal.
dissolve	
10 grs. sulphate of alumina	1lb.
3 grs. chlorate of potash or soda	5oz.
2 grs. sal ammoniac	3oz.
Then mix with	
50 grs. gumwater, 1 to 1	½ gal.

Catechu (Cutch) Solution, 20° *Tw.*

To	
1 litre boiling water	1 gal.
add	
600 grs. catechu previously broken up	6lbs.

Stir and heat until all the lumps have disappeared, then leave to cool and settle, and make up the liquor to 20° Tw.

The sediment is treated with hot water, and the liquor after cooling and settling is separated, and used in dissolving a fresh lot of catechu. This colour is often modified by the addition of extracts of red or yellow dyewoods, as for instance to the above proportions of Brown No. 1 the following may be added :—

5 grs. Sapan extract, 30° Tw.	½lb.
10 grs. quercitron extract, 30° Tw.	1lb.

and if necessary more gum thickening according to shade required.

Steam Catechu.—No. 2.

100 grs. catechu solution, 20° Tw	1 gal.
100 grs. water	1 gal.
10 grs. dark British gum	1lb.
25 grs. starch.	2½lbs.

Boil, stir till cold, then add

100 grs. chlorate of chrome, 20° Tw .... 1 gal.

Catechu Solution, 20° *Tw.*

In

1000 grs. (1 litre) boiling water .... 1 gal.

dissolve

500 grs. catechu (in cubes) .... 5lbs.

then add

200 grs. acetic acid, 10° Tw. .... 2lbs.

then filter.

It is generally advisable, in patterns containing much of this brown, before exposing to steaming, to pass the pieces through a steam ager, which will decompose the chlorate of chrome and take away the liberated chloric acid, which would otherwise react on the cloth; but this special method of fixation will be mentioned again when speaking of aniline black and other oxidation colours.

Neither of the above steam catechu browns require chroming for the development of the shades, as the oxidation is effected through the process of steaming by the chlorate. The oxidation can also be effected by means of copper salts, and, in fact, a very old method of the fixation of catechu browns on calico by printing relies on the employment of copper salts. Steam catechu browns are also produced with acetate of chrome and chlorate of soda or potash in the same way as a logwood steam black, and it is here to be observed that a great variety of brown shades can be produced in which the catechu brown is modified by the addition of Sapan, quercitron, or logwood extract, and in many cases for cheapness sake, instead of the redwood extracts, magenta or one of the cheap aniline red colours generally obtained as bye-products in the magenta manufacture can be employed. The following recipe can be taken as an example :—

Steam Catechu Brown.—No. 3.

100 grs. catechu solution, 20° Tw.	1 gal.
200 grs. Sapan liquor, 30° Tw.	2 gal.
50 grs. magenta solution (3 per cent.)	½ gal.
25 grs. logwood liquor, 30° Tw.	¼ gal.
10 grs. acetic acid, 11° Tw.	1lb.
50 grs. starch.	5lbs.

boil, and while still hot, add

4 grs. chlorate of soda or potash	6oz.

stir until cold, then add further :

40 grs. acetate of chrome, 35° Tw.	4lbs.
40 grs. basic chlorate of chrome, 18° Tw	4lbs.
24 grs. nitrate of alumina, 20° Tw	2½lbs.

Basic Chlorate of Chrome.

In

150cc. boiling water	1½gal.

dissolve

50 grs. chlorate of barium	5lbs.

then add

35 grs. chrome alum.	3½lbs.

Stir until dissolved, and then add

20 grs. precipitated hydrate of chromium oxide.	2lbs.

Mix, leave to settle twelve hours, then filter.

The following colours require a passage through bichromate of potash for their development, and are connected with other steam colours which will stand chroming.

Steam Catechu Brown.—No. 4.

100 grs. catechu liquor, 20° Tw.	1 gal.
10 grs. acetate of soda	1lb.
300 grs. gum water	3 gal.
30 grs. Persian berry extract, 15° Tw	3lbs.
35 grs. acetic acid	3½lbs.
20 grs. acetate of manganese, 30° Tw.	2lbs.
20 grs. acetate of alumina, 20° Tw.	2lbs.

This colour is printed along with other steam colours, is then steamed in the usual way, and fixed or raised by passing through a 3 per cent. bichromate of potash solution at about 70° C. for three to five minutes, or can be passed through two bichrome baths as follows :

First bath :

1 litre boiling water	10 gal.
30 grs. bichromate of patash or soda	3lbs.
25 grs. common salt	2½lbs.

Second bath :

1 litre water at 65° C to 70°	10 gal.
30 grs. bichrome	3lbs.
25 grs. common salt.	2½lbs.
5 grs. alum	½lb.

The cloth is passed for one minute in each bath, then thoroughly washed. In some cases a cold bichromate solution can be employed, but it must be taken stronger.

Steam Catechu Brown.—No. 5.

100 grs. catechu liquor, 20° Tw.	1 gal.
200 grs. gum water.	2 gal.
20 grs. acetate of alumina, 20° Tw.	2lbs.
2 to 5 grs. nitrate or acetate of copper.	5 to 8 oz.

Print, steam, age, and pass through bichrome.

In preparing catechu solutions sometimes caustic soda is employed, as for instance:—

100 grs. caustic lye, 15° Tw.	1 gal.
100 grs. water	1 gal.
80 to 100 grs. catechu	8 to 10lbs.

After separating from the sediment the solution is thickened with the necessary amount of gum water, then printed, steamed, and chromed as mentioned before.

Another method of fixing cutch shades without steaming is by ageing and then passing through a lime water, and in this case the bichrome bath is dispensed with, the colour being prepared for this purpose with copper salts, for instance—

100 grs. cutch liquor, 20° Tw.	1 gal.
100 to 200 grs. gum water	1 to 2 gal.
10 grs. sal amoniac	1lb.
1 gr. verdigris	1½oz.
20 grs. acetate of lime solution	2lbs.

COMPOUND SHADES.

As already mentioned, the dyewood extracts give rise to a great variety of compound shades, amongst which browns, olives, chocolates, etc., can be mentioned. It has already been seen in the case of cutch browns that the shades can be greatly modified by the addition of other dyewood extracts. Knowing the shades obtained with the different dyewood extracts, and also those produced with the different mordants, we can easily imagine that there is no limit in the production of compound steam colours, the more so as not only the dyewood extracts can be used and mixed with each other, but can be connected with coal tar colours, principally those of the alizarin class, and in many cases also the anilines. In the production of these compound colours we have therefore as mordants principally alumina, iron and chromium acetates; and as dyestuffs, logwood, yellow and red wood extracts, without speaking of alizarin, etc.

Olive Shades.

A very useful class of compound shades are the olive greens, which are largely employed in steam colour printing, and are mostly produced by means of logwood and quercitron, or berry extracts, acetate of chrome being mostly employed as the mordant; in other words, the colours are prepared in almost the same way as the logwood blacks, with the exception that the proportions are different. The amount of thickening is of course much larger, while the proportions of logwood and yellow extract will vary according to the shade required. The logwood preparations already found in the market as steam blacks or steam indigo substitutes will be found very useful for the production of olive shades. Persian berry extract connected with aluminium and iron mordants gives already olive shades.

The following recipe may be taken as an example for the production of olives.

100cc. water	1 gal.
30 grs. Persian berry extract, 45° Tw.	3lbs.
10 grs. logwood extract, 45° Tw.	1lb.
2 grs. olive oil	4oz.
10 grs. starch	1lbs.

boil, stir, until cold, then add

20 grs. acetate of chrome, 25° Tw.	2lbs.

As will be readily understood, in this recipe the preparation of the logwood or berry extracts can be altered according as a greener or a yellower olive is required. Instead of the berry the bark extract can also be employed, and the shade can be modified by means of an aniline colour, such as methylene blue or green. The addition of acetate of iron to the colour will also modify the shade.

Compound Brown and Chocolate Shades.

The browns very often contain catechu, and have already been mentioned, while chocolates are generally produced by means of Sapan extract and acetate of chrome, the shade being modified according to requirement by means of logwood, quercitron extract, etc. The following recipes may serve as illustrations for compound shades:—

Sapan Brown.

100 grs.	bark liquor 10° Tw.	1 gal.
50 grs.	Sapan liquor, 10° Tw.	½ gal.
10 grs.	logwood liquor, 10° Tw.	1lb.
50 grs.	British gum	5lbs.
½ grs.	chlorate of potash or soda	¾oz.
7½ grs.	alum	¾lb.

Boil, then add

2 grs.	red prussiate of potash	3oz.
1 gr.	oxalic acid	1½oz.

Chocolate.

100 grs.	Sapan liquor, 10° Tw.	1 gal.
50 grs.	logwood liquor, 10° Tw.	½ gal.
20 grs.	bark liquor, 10° Tw.	2lbs.
50 grs.	red liquor (acetate of alumina), 15° Tw.	½ gal.
20 grs.	starch	2lbs.

Boil; when nearly cold, add

2 grs.	chlorate of soda	3½oz.
1 gr.	red prussiate of potash	1¾oz.
2 grs.	yellow prussiate of potash	3½oz.

Stir until all is dissolved.

The chlorate of soda will dissolve readily in the colour, and it will be advisable to grind the red and yellow prussiates to a fine powder before adding them.

Since the lowering in price of artificial alizarin the chocolates derived from the red dyewood have lost a great deal of their importance, the more so as for the production of these chocolates with alizarin, old red or purple colours of the printworks are mixed together, the shade being modified according to requirement by the addition of dyewood extracts, etc. The extracts of dyewoods are also very extensively used for the production of fancy or light shades of great variety, such as lavender, lilacs, cream, etc., or in other words, for producing very light and in fact tinted shades as ground or blotch for other patterns.

STEAM MINERAL COLOURS.

Although only a few, these have attracted considerable attention in the last few years, and some are found to be of great utility in printing. Up to a few years ago steam Prussian blue and one or two others were the only representatives of this class of colours, which, however, have now been increased by the addition of several others.

STEAM CHROME YELLOW.—*No.* 1.

In

50 grs. tragacanth water (20 per cent)............ 5lbs.

dissolve

40 grs. nitrate of lead .... 4lbs.

then cool and add

100 grs. chromate of barium paste (50 per cent.) 10lbs.

Print, dry, and steam in the usual way, when the yellow will be fixed on the fibre; the colour stands boiling soap well. The chromate of barium is produced by adding bichromate of soda or potash solution to a solution of chloride of barium, until no more precipitate is formed. It is then filtered and the precipitate allowed to drain until it contains 50 per cent of dry colour. This method is due to H. Schmid.

Steam Chrome Orange.

50 grs. thickening	5lbs.
50 grs. nitrate lead	5lbs.
75 grs. acetate of lead	7½lbs.
150 grs. chromate of barium, 50 per cent.	15lbs.

Another method for the production of steam chrome yellow consists in the employment of chlorate of chromium, but this method is not largely used, because in some cases the cloth may be tendered during the steaming.

Steam Chrome Yellow.—No. 2.

100 grs. chlorate of chromium, 20° Tw.	1 gal.
25 grs. acetate of lead.	2lbs.
10 grs. ly-chô.*	1lb.

are mixed in the cold. This colour yields a greenish yellow, which does not tender the fibre like the following one:—

Steam Chrome Yellow.—No. 3.

125 grs. chlorate of chrome, 20° Tw.	1¼ gal.
20 grs. acetate of lead	2lbs.
10 grs. ly-chô.	1lb.

This method is recommended by Dépierre and Tatarinoff, and can be employed even on indigo dyed goods when the discharge is effected at the same time that the colour is fixed.

After printing the yellow No. 2, and steaming by passing through milk of lime, the yellow is converted into orange; the No. 3, however, while giving a good yellow and discharging the indigo well, does not yield an orange afterwards.

STEAM CADMIUM YELLOW.—*No.* 1.

To

100 grs. thickening (preferably tragacanth water, 20 per cent.)	1 gal.

add

30 grs. nitrate of cadmium	3lbs.

previously mixed with

30 grs. hyposulphite of soda	3lbs.

Leave to stand a couple of days before printing, then steam, etc.

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* Ly-chô or ly-chow is a white grey powder, produced in French works near Rouen, and is very probably only a starch lightly calcined; it is rather an expensive product, but being a good thickener is used for special purposes.

Nitrate of Cadmium

can be easily prepared by dissolving the commercial cadmium metal in bars in ordinary nitric acid ; the solution takes place at the ordinary temperature, and the nitrate of cadmium can then be obtained from the solution by crystallisation. Although cadmium is a pretty expensive metal, it can be employed for this purpose at a remunerative price.

It must be remembered that cadmium nitrate is sometimes employed in steam pigment chrome yellows, fixed by albumen along with the lead chromate and a certain amount of acetate of soda, in order to prevent the injurious effect of sulphuretted hydrogen, which is sometimes produced during the steaming of albumen colours.

The cadmium yellow or cadmium sulphuret has the advantage over lead chromate in not blackening when exposed to sulphuretted hydrogen fumes, a drawback always attached to lead compounds.

Steam Cadmium Yellow.—No. 2.

This is a modification of the No. 1.

100cc. water	1 gal.
20 grs. starch	2lbs.
20 grs. tragacanth water (20 per cent.)	2lbs.

Boil, and while still hot add

45 grs. hyposulphite of soda	4½lbs.

stir until all is dissolved, then add

45 grs. nitrate of cadmium	4½lbs.

mixed with

20 grs. water	2lbs.

Stir until all is in solution, print, dry, and steam 1 to 1½ hours.

The colour can be tinted with an azo colour solution in order to make it apparent while printing.

Steam Cadmium Yellow.—No. 3.

100 grs. thickening (preferably tragacanth)	1 gal.
20 grs. precipitated sulphur	2lbs.
15 grs. arsenious acid	1½lbs.
30 grs. nitrate of cadmium	3lbs.
45 grs. acetate of soda	4½lbs.

Strain several times through sieve, print, and steam one hour. This colour can be easily kept, and is not liable to run, provided no excess of acetate of soda be used; the arsenious acid is removed by washing and soaping the pieces. This yellow is pretty fast, although not quite as fast against light as chrome yellow. It can be connected with alizarin, orange, malachite green, methylene blue, etc.

Another yellow, which might to a certain extent be employed in printing, is the zinc chromate, which, according to Barreswill, can be dissolved in ammonia, printed, and fixed on the fibre simply by exposure to air, when the ammonia evaporates and leaves the yellow behind.

IRON BUFF.

This can scarcely be called a steam colour, although it is sometimes connected with other steam shades. It is simply the acetate of iron thickened and printed; by ageing or hanging the acetic acid is driven off, and the oxide is then fixed on the fibre, while at the same time oxidation takes place, the ferrous oxide being converted into the ferric. It belongs, therefore, more to the class of mordants, or oxidation shades, than to the steam colours. The following may be taken as an example:—

Buff Standard.

In

1 litre boiling water	1 gal.

dissolve

550 grs. copperas (sulphate of iron)	5½lbs.
440 grs. acetate of lead (sugar of lead)	4½lbs.

then leave to settle, filter, and keep the solution in closed bottles or carboys, for use. The standard is made up to 30° Tw.

Dark Buff.

100 grs. buff solution, as above, 30° Tw.	1 gal.
100 grs. dextrin or starch thickening	1 gal.

for lighter shades use more thickening.

Light buffs are frequently used as ground for differently coloured designs, being very often padded or blotched over already printed pieces. As a rule, buffs, after printing and ageing, are, so to say, fixed by means of a chalk bath, at about 75° C., containing

10 grs. chalk	1lb.

for

1 litre water	10 gal.

The basic iron mordant prepared with ammonia can also be used for the productions of buffs in printing.

STEAM PRUSSIATE BLUE.

This colour has lost much of its importance since the introduction of coal tar colours; it is, however, still pretty largely employed in printworks, where it is found very useful for some special purposes.

Steam Prussiate Blue.—No. 1.

100 cc. water	1 gal.
10 grs. starch	1lb.

boil, while still hot add

2 grs. sal ammoniac	3¼oz.

stir until dissolved, then add, when cold

120 grs. tin pulp	12lbs.

Mix well, then add further

20 grs. red prussiate of potash	2lbs.
60 grs. yellow prussiate of potash	6lbs.

(both in fine powder)

Mix well, and next morning add

8 grs.	pulverised tartaric acid crystals	12oz.

and a solution of

5 grs.	oxalic acid	8oz.

in

10 cc.	water	1lb.

Prussiate of Tin Pulp.—No. 1.

Dissolve

10 grs.	yellow prussiate	1lb.

in

100 cc.	boiling water	1 gal.

then filter and cool.

No. 2.

Dissolve

10 grs.	tin crystals	1lb.

in

100 cc.	hot water	1 gal.

filter and cool. Add Nos. 1 and 2 together, stir well, then leave to settle, and filter, leave the pulp to drain until about

100 grs.	pulp	1 gal.

are obtained.

A simpler method of mixing the steam prussiate blue No. 1, is the following:—Boil the starch and chlorammonium in the water, and while still hot add the other ingredients, the yellow and red prussiate, and tartaric acid, in fine powder, then the solution of oxalic acid in water, and when cold, before printing, add the prussiate of tin pulp. This blue can be printed on cloth previously prepared with oleine, or, better, with stannic acid.

The preparation of cloth with stannate of soda and sulphuric acid before printing, with some steam colours, is very much in vogue even now, but perhaps not so much as it was some years ago, since cloth prepared with oleine is being so largely used now for printing on, with steam colours, from coal tar derivatives.

For preparing cloth with stannate of soda and sulphuric acid, the proportions of each bath vary according to the depth of shades which are afterwards printed, but the following may serve as a guide:—

The pieces are treated with a solution of stannate of soda at about 10 to 12° Tw.; after removing from the bath they are allowed to stand for one hour, and treated again with the stannate of soda, and afterwards passed through sulphuric acid bath, showing 2 to 4° Tw., then washed and dried. It has been found by long experience that brighter and even faster colours are produced. For deep shades the stannate of soda is taken, even stronger, say 20 to 24° Tw., while the acid bath is taken so as to show 6° Tw., or better, to show the corresponding amount of free sulphuric acid. After printing the cloth, the Prussian blue is dried, steamed 45 minutes to one hour without pressure, aged, and then passed for five minutes in bichromate of potash bath, at about 120° F., containing 5 grs. per litre (½lb. per 10 gallons). After this, it is washed and dried.

Prussiate blues can be connected with Persian berry or quercitron yellow for the production of steam greens, as, for instance:—

Dark Steam Green (with Prussiate.)

100 cc. Persian berry liquor at 10° Tw	1 gal.
5 cc. logwood extract, at 10° Tw.	½lb.
15 grs. starch	1½lb.
10 grs. powdered alum	1lb.
50 grs. yellow prussiate	5lbs.

Boil, and when cooled down to 50° C. add a mixture of

10 grs. strong sulphuric acid	1lb.
5 grs. water	½lb.

mix well, and add, when quite cold

15 grs. prussiate of tin paste	1½lb.

Print and steam in the usual way as for prussiate blue.

Another dark green, originally obtained by Havraneck, from whom it has taken its name, is the following:—

Steam Havraneck Green.

100 grs. hot starch thickening	1 gal.

dissolve

5 grs. red prussiate	½lb.
15 grs. yellow prussiate	1½lb.
7½ grs. chrome alum	¾lb.
5 grs. tartaric acid	½lb.

STEAM MANGANESE BROWN.

This method has been recommended by Balanche, and will, no doubt, be found very useful for the production of manganese brown or bronzes by a direct process capable of being connected with other steam colours; the shades produced are absolutely fast against light and soap. The printing colour, as originally recommended, is prepared as follows :—

Steam Manganese Brown.

100 grs. water	1 gal.
20 grs. starch	2lbs.
20 grs. bichromate of potash	2lbs.

Boil, stir until cold, then add

25 grs. chloride of manganese	2½lbs.

and

25 grs. acetate of soda solution at 25° Tw	2½lbs.

Instead of the bichromate of potash, the sodium salt may be advantageously employed; it is, in fact, to be preferred, being not so apt to crystallise in the colour as the potassium salt. Print, dry, and steam, when a very deep brown is obtained, which stands soaping at the boil. For brighter shades the above colour must be reduced with more thickening. Instead of thickening with starch, dextrin may be employed. In this case the bichromate of soda is dissolved in hot water, and a sufficient amount of dextrin is added to produce a properly thickened colour, and, when cold, the acetate of soda and manganese chloride are added

Bismuth and antimony have been recommended for the production of steam printing colours, the first for a brown or bronze, the second for an orange, both being produced as sulphides on the fibre ; but they are scarcely ever, if at all, used in printworks for these purposes. The colours produced by copper are not of great practical interest, although the phosphate of copper green, as recommended by C. Kœchlin, might be found in special cases to be useful. The fixation of other metallic compounds has likewise not been found of much utility.

STEAM PRINTING COLOURS,

OR

PROCESSES OF RECENT INTRODUCTION.

Casella's New Blue for Printing R. and B.

50 grs. hot thickening	5lbs.
2 grs. new blue	3oz.
10 grs. acetic acid	1lb.

Mix well, keep the temperature at about 170° F., or 75 to 80° C., until the colour is completely dissolved, then cool and add:—

5 grs. tannic acid	8oz.
15 grs. acetic acid 8° Tw.	1½lbs.
2 grs. tartaric acid	3oz.
20 grs. water	2lbs.

then dilute with acetic acid in order to have in all

100 grs. colour	1 gal.

For deeper shades add more dyestuff, say

5 grs. new blue	8oz.

instead of the proportion given above, and increase the amount of tannic acid to

7½ grs. tannic	12oz.

Print, dry at moderate heat, steam for about one hour, and pass through tartar emetic at 75° C., 170° F.; the bath being made up with about

5 grs. tartar emetic	1oz.

per

1 litre water	1 gal.

Wash well, then soap as usual.

Thickening for above.

20 grs. tragacanth gum	1lb.
dissolved in	
200 grs. water	1 gal.
200 grs. wheat starch	10lbs.
stirred with	
300 grs. water	1½ gal.
100 grs. acetic acid	½ gal.
diluted with	
300 grs. water	1½ gal.

Boil half-an-hour, and stir until cold.

Indigen Blue—from the Bäyer Colour Works, Elberfeld.

100 grs. starch paste (12 to 15 per cent.)	1 gal.
5 grs. citric acid	8oz.
7½ grs. alcohol	10oz.
7½ grs. oleine solution 1 to 10	10oz.
10 to 15 grs. indigen paste	1¾lbs.
7½ grs. tannic acid solution (60 per cent.)	10oz.

Print, dry, steam as usual, and follow with the customary tartar emetic bath and soaping.

Indulin Paste—from the Hœchst Colour Works.

This blue is brought into the market of three shades, R., B and B B.

1.—*Tragacanth Thickening.*

100 grs. tragacanth	1lb.
1000 grs. water	1 gal.

2.—*Starch Thickening.*

Boil well	
20 grs. starch	2lbs.
100 grs. water	1 gal.
then add	
20 grs. of above tragacanth thickening	2lbs.

Stir until cold

3.—*Acetic Starch Thickening.*

Mix	
100 grs. above starch thickening	1 gal.
with	
40 grs. acetic acid (50 per cent.)	4lbs.

4.—*Tannic Acid Solution.*

Dissolve	
100 grs. tannic acid	10lbs.
in	
100 hot tragacanth thickening	1lb.

Stir until dissolved and cool.

5.—*Oil Emulsion.*

Boil	
25 cc. soapwort	2½lbs.
in	
100 cc. water	1 gal.
and the decoction made up to	
100 cc. solution	1 gal.
to this add	
600 grs. olive oil.	6 gals.

and stir until a good emulsion is produced.

6.—*Preparation of the Dyestuff.*

Mix	
100grs. of the 25 per cent. paste	1lb.
with	
75 grs. tragacanth thickening	¾ gal.

by grinding them together in a mortar or in a mill until intimately mixed.

7.—*Ethyl Tartrate.*

Equal parts of pulverised, sharply dried, tartrate (or tartaric acid) and pure alcohol are heated at 70° C,, until the acid is completely dissolved, in an enamelled iron vessel provided with agitator and inverted condenser. The product forms an article of commerce.

8.—*Colour for Printing,*

63 grs. acetic starch thickening	1 gal.
6½ grs. ethyl tartrate	1lb.
7½ grs. oil emulsion	1lb.
11½ grs. preparation of dyestuff	3lbs.
10 grs. tannic acid solution in tragacanth gum..	4½lbs.

Print on oiled cloth, steam 1½ hours in moderately moist steam (dry steam blackens the colour and steam too moist does not develop it sufficiently). After steaming pass goods not folded (on the cylinder,) direct through chalk or cowdung, malt, or soap.

The printed patterns of red and blue are mostly produced by printing with natural indigo on Turkey red dyed cloth, by means of the glucose process. To imitate goods thus produced some cheaper methods have been followed, which, however, have not produced such fast results as by means of the indigo. But among other methods one lately introduced has given very fair results, the deep blues obtained by this process on Turkey red grounds being very close imitations of those produced by means of indigo. The process consists in the preparation of a steam blue composed of a paste of the colouring matter, and of another paste containing the mordant or fixing agent, the method recommended for application being the following:—

Dark Blue.

25 grs. blue paste	2½lbs.
100 grs. preparation of mordant	10lbs.
50 grs. starch paste	5lbs.
4 grs. acetate of soda	6½ozs.

Mix well until dissolved.

Medium Blue.

25 grs. blue paste	2½lbs.
75 grs. preparation	7½lbs.
75 grs. starch paste	7½lbs.
4 grs. acetate of soda	6½oz.

Light Blue.

20 grs. blue paste	2lbs.
75 grs. preparation	7½lbs.
100 grs. starch paste	10lbs.

Print on Turkey red dyed cloth, steam from three quarters of an hour to one hour; then pass for three to four minutes in warm bath containing

15 grs. tannic acid	2½oz.
Per 1 litre water	1 gal.

Then wash well and dry. By this method very good imitations of indigo blue on Turkey red are produced, which stand soaping fairly well.

Two new dyestuffs have been introduced by the Badische Anilin and Soda Fabrik. One is the galloflavine yellow, the other the anthracene brown; both being introduced in commerce as 20 per cent pastes, and capable of being employed in dyeing or printing by the same methods as alizarin. The following recipes may be taken as examples:

Galloflavine Yellow.

Thickening.

100 grs. water	1 gal.
15 grs. starch	1½lbs.
30 grs. tragacanth water (60 : 1000)	3lbs.
5 grs. olive oil	½lb.

Printing Colour.

12 to 14 grs. galloflavine paste	1¼ to 1½lbs.
2grs. acetic of chrome, 30° Tw.	4oz.
6 grs. acetic acid, 10° Tw.	½lb.
100 grs. thickening	1 gal.

Print on ordinary or oleine prepared cloth, dry, steam as for alizarin, then wash and soap. Instead of the chromium acetate the alumina mordant can be used, when a brighter yellow is produced. A brighter colour is also produced if, after printing and steaming, the cloth be passed through a bath containing tin chloride, but it loses somewhat in fastness. The yellows produced by galloflavine are not so bright as those obtained by chromate of lead, but they may nevertheless be found useful, on account of their capability of being used as steam colours along with alizarin and other fast shades. With iron mordants galloflavine produces very pretty olive colours, which will no doubt be found useful in calico printing, and the colouring matter may also be connected with others for producing a great variety of compound colours.

The anthracene brown is likewise introduced in commerce in the paste form; it yields fast colours if applied in the same way as alizarin, with alumina or chromium mordants, as reddish brown with the former and a tobacco brown with the latter.

Anthracene Brown.

The cloth is previously oiled in a bath containing

100 grs. water	2 gals.
1½ grs. soda crystals	2½oz.
5 grs. alizarin oil	1lb.

Thickening.

100 grs. water	1 gal.
15 grs. starch	1½lbs.
30 grs. tragacanth solution	3lbs.
5 grs. olive oil	½lb.

Printing Colours.

No. 1, with Chromium Mordant.

20 grs. anthracene brown	2lbs.
12 grs. acetate of chrome, 30° Tw.	1½lbs.
6 grs. acetic acid	½lb.
100 grs. thickening	1 gal.

No. 2, with Acetate of Alumina.

20 grs. anthracene brown	2lbs.
20 grs. acetate of alumina 15° Tw.	2lbs.
6 grs. acetic acid 10° Tw.	½lb.
100 grs. thickening	1 gal.

Print, dry, steam as with alizarin, wash and soap. The colour can be also applied in cotton dyeing by employing the same mordants as with alizarin red. I am obliged for these recipes to the respective Manchester agents of the above firms.

Steam Dinitroso Resorcin Olive.

200 grs. dinitroso resorcin paste.
½ litre acetic acid 10° Tw.
¾ litre tragacanth water.
15 grs. nitrate of iron, 70° Tw.
30 grs. acetate of magnesia, 40° Tw.
60 grs. acetate of chrome, 30° Tw.

Print on oleine prepared cloth, steam, wash, and dry. The shade thus obtained stands boiling soap. This new product has been also employed in dyeing on iron mordant, being afterwards discharged by means of tin salt, as will be mentioned later on. It is also employed for black dyeing or cloth mordanted with sumach and iron, in connection with other dyestuff. For this recipe I am obliged to Mr. Horace Koechlin.

NEW METHODS OF DISSOLVING ANILINE COLOURS.

Acetine.

The Badische Anilin and Soda Fabrik has just taken out a patent for preparing solutions of basic colouring matters for printing purposes by means of the acetines, aceto-chlorhydrines, and the chlorhydrines of glycerine. Practically, the product mostly employed, and which is described as *acetine,* is a mixture of mono and diacetine, and is obtained by boiling for 48 hours, in a flask or vessel connected with an inverted condenser, glycerine with double its weight of glacial acetic acid, and afterwards distilling off the acetic acid which has not entered into the reaction.* These glycerine ethers can be employed in printing by two methods; they are either utilised for preparing solutions of aniline colours, or simply added when the printing colours are prepared. The following recipes may be taken as examples:

N1.

50 grs. induline	10lbs.
200 grs. acetine	40lbs.

are heated four hours at 80 to 90° C., until the solution is complete

15 grs. induline solution, as above	1½lb.
100 grs. starch paste	10lbs.
4 to 5 grs. tannic acid	½lb.

N2.

10 grs. induline paste, 20 per cent.	1lb.
77 grs. thickening	7½lbs.
3 grs, tannic acid	6½oz.
10 grs. acetine	1lb.

When the acetines (or the other water soluble ethers of glycerine) are employed. it is unnecessary to add acetic acid to the printing colour; but when the ether is not easily soluble, as in the ease of the triacetine, aceto-chlorhydrine, and dichlorhydrine, it is well to add to the preparation a small amount of acetic acid. The best results, however, are obtained with the solutions of the colouring matters in acetine, previously prepared.

Lævulinic Acid.

For the same purpose of fixing aniline colours in printing, the Oechst Colour Works have patented the employment of

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* Some years ago the author, in working with indulines, obtained a solution, by heating for a long time, induline, glycerine, and glacial acetic acid, but as the temperature employed was not very high, no strong solution was produced.

lævulinic acid, and have brought out a preparation under the name of lævuline blue, which is a syrupy solution of induline in lævulinic acid. In employing this latter solvent better results are also claimed than by the methods used before, when fixing colours by the tannic acid process, in which the lævulinic acid replaces the other and more expensive organic acids, such as tartaric or oxalic acids, etc., with advantage. It can even be employed in the preparation of alizarin and other steam colours in place of acetic acid, when chromium or alumina mordants are used.

Of the new additions to the azo colours, the Congo red, benzopurpurine, and chrysamine, etc., application has already been made of them in printing, the colours being applied in a potash solution properly thickened and then fixed by steaming.

THE OXIDATION COLOURS.

These form a very interesting class of dyestuffs, which differ from the others previously treated in the fact that they are not found in commerce as ready finished products, but are produced on the fibre itself by oxidation.

Aniline black is the most important of this series, and there is no doubt that other shades or colours can be produced on the same principle of oxidation on the fibre, along with those already existing, the principal of which are the following :—

ANILINE BLACK.

Several methods are followed in practice, all relying on the oxidation of an aniline salt (mostly the hydrochlorate) with a chlorate and a metallic compound, which acts as oxygen carrier. For the latter, copper, vanadium, chromium cerium, and iron compounds have been employed. The principle of the preparation of the aniline black colours is, that besides the thickening, which is generally starch paste, with or without British gum, the preparation must contain :

An aniline salt,
Chlorate of soda or potash,

and the metallic compound mentioned before. For this latter those which are mostly employed are :

Sulphide of copper.
Sulphocyanide of copper.
Bivanadiate of ammonia.
Insoluble chromates, such as chrome yellow, &c.
Yellow and red prussiates.

The latter two allow of the preparation of so-called steam aniline blacks, which permit the colours to be exposed to a certain amount of steaming, while by means of the other products the colours require ageing for their development. The systems of ageing vary considerably in the different works, some simply using stoves which are heated by means of steam pipes, and the atmosphere kept moist by the injection of steam. Special ageing rooms have been constructed in some works, in which the temperature is kept at about 100° F. with the dry bulb thermometer, thus showing 94 to 95° F. on the wet bulb.

The cloth is passed through these ageing-rooms or machines up and down several times through a system of rollers, over which it takes from 15 to 28 minutes to travel. The goods are then left in bundles in a warm room over night, or sometimes even longer, when the oxidation which had been started in the ageing machine is continued, and thus the black is properly developed. One of the newest apparatus for the ageing of cloth printed aniline black is the steam ager of Messrs. Mather and Platt (Plate VII.), which is coming more and more prominently into use.

The cloth is passed through this ager at the rate of 60 yards per minute, being exposed to the action of the steam for about one minute at a temperature of about 185° F. while passing up and down, over a system of rollers, as shown in the illustration.

In the laboratory it is rather difficult to age patterns which have been printed with aniline black; in fact, in some cases it is almost an impossibility when no steam is at hand. The black may, however, be developed by a very short steaming in the neck of a glass flask, in which the water is kept at a brisk boil by means of a Bunsen burner. The printed and dried cloth is wrapped up in some grey cotton cloth and made into a thick roll, which is introduced into the neck of the flask, taking care, of course, that the lower end does not touch the water. From two to five minutes steaming is in this case sufficient for developing or rather for starting the development of the black, which is then completed, by allowing the patterns to remain hung or wrapped up for some time.

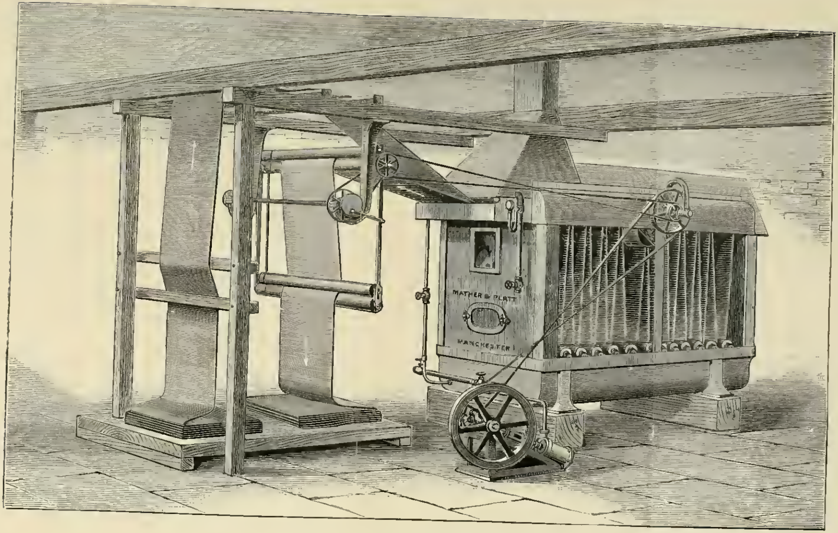

PLATE VII.—STEAM AGER.

In the preparation of colours for aniline black printing, either the commercial aniline oil or the aniline salt is employed.

In using the oil, as a rule, about equal volumes of aniline oil and hydrochloric acid are mixed together; but it is well to neutralise as much as possible, in order not to have any excess of acid, which would act injuriously and might tender the cloth.

For this reason, when the acid is added to the aniline oil, a test paper or a test solution of methyl violet is used to act as indicator; so long as there is any excess of acid a drop of the mixture applied on the test paper (which is simply blotting paper soaked in a solution of methyl violet and dried) will turn the violet into green, which will be visible round the spot where a drop of the mixture has been applied. The same takes place if a drop of the acid and aniline mixture is added to a weak methyl violet solution, which will be turned into green if the hydrochloric acid is in excess. As a rule the acid is added to the aniline oil until it shows a slight excess, which is then neutralised by the addition of more aniline oil. In some works it is the rule to add a small quantity of aniline oil in excess, to the aniline black colour, in order to make sure that there is no free acid.

The following recipes may be taken as examples of the preparation of aniline black colours:—

Sulphide of Copper Black.

No. 1.

100 cc. water	1 gal.
10 grs. starch	1lb.
5 grs dextrin	½lb.

Boil, and while still hot, add

20 grs. aniline salt	2lbs.
1½ grs. aniline oil	2oz.

Stir until cold.

No. 2.

In another vessel boil

100 cc. chlorate of soda solution, 12° Tw.	1 gal.
10 grs. starch	1lb.
5 grs. dextrin	½lb.
5 grs. sal ammoniac.	⅔lb.

Stir until cold.

Mix Nos. 1 and 2 together, then add, before printing,

15 grs. sulphide of copper paste	1½lbs.

Print, dry, age, leave in bundle all night, then soap, etc.

Sulphide of Copper Paste.

In

100 grs. caustic soda, 10° Tw.	10lbs.

dissolve cold

20 grs. flowers of sulphur	2lbs.

stir occasionally until all is dissolved, which will take upwards of 24 hours, then add

100 grs. sulphate of copper	10lbs.

previously dissolved in

2 litres boiling water	20 gal.

wash the precipitate by decantation, filter, wash on filter until filtering liquor is neutral, and leave to drain until it measures about

100 cc.	1 gal.

This was one of the first processes employed in the printing of aniline black, and was recommended by Lauth. It must be observed that, in the case of copper sulphide and also of the other metallic oxidisers, they should be added only before printing, as the colours do not keep long, and they deteriorate by standing.

Sulphocyanide of Copper Black.

100 grs. water	1 gal.
7½ grs. starch	¾lb.
10 grs. dextrin	1lb.

Boil, and while still warm add

10 grs. aniline salt	1lb.

stir until cold, then add

5 grs. chlorate of soda, in fine powder	½lb.

stir until dissolved, and before printing add

1½ grs. sulphocyanide of copper paste	2oz.

In all recipes for aniline black, the aniline oil can be employed instead of the salt if the precaution be taken of well neutralising by means of hydrochloric acid, using methyl violet as an indicator. A certain amount of sal-ammoniac is very often employed in the colour in order that it may attract moisture in the ageing room, and thus help in the oxidation.

Black with Vanadium.

100 grs. water	1 gal.
15 grs. starch	1½lbs.
7½ grs. dextrin	¾lb.

Boil, cool down to 120° F., then add

15 grs. aniline oil	1½lbs.

previously neutralised with about

15 grs. hydrochloric acid 32° Tw	1½lbs.

stir until cold, then add cold solution of

7½ grs. chlorate of soda	¾lb.

dissolved previously in

10 cc. boiling water	1lb.

Before printing add further

5 grs. vanadium solution	½lb.

print, dry not too hard, age two days, then pass through 2 per cent. solution of bichromate of potash at about 160° F., wash and soap.

Vanadium Solution.

7½ grs. bivanadiate of ammonia	1oz.

are dissolved in

40 grs. water	6oz.

and

40 grs. hydrochloric acid 30° Tw.	5oz.

add

5 grs. glycerine	¾oz.
20 grs. water	4oz.

heat the whole until the green solution becomes intense blue, and then dilute with water to make it up to

1 litre	1 gal.

and keep in bottles for use.

This method by means of vanadium solution (for which also sometimes simply bivanadiate of ammonia as such is taken) is now largely employed, especially in this country, in spite of the high price of the product, but the relative quantity used is so small that the prime cost of the vanadium salt is completely out of the question. A small quantity of the vanadium compound is found to be very effective, it having been proved by experiment that one part bivanadiate ammonia is capable of oxidising as much as 60 to 70,000 parts of thickened aniline black colour.

In printing aniline blacks, printers very often add a small amount of lamp black for the purpose of sighting or of making evident the patterns after having been printed.

Prussiate Aniline Black.

This method is due to Cordillot, and constitutes the first steam aniline black introduced in practice, and the process would be very valuable if it were not so expensive.

100 grs. water	1 gal.
15lbs. starch	1½lbs.
7½ grs. dextrin	¾lb.
1 gr. lampblack	1½oz.
20 grs. anilin oil.	2lbs.

Boil, then add

12½ grs. chlorate of barium	1¼lbs.

stir until dissolved, then add in small portions at a time

25 grs. tartaric acid	2½lbs.

dissolved in

45 grs. water	4½lbs.

Mix well, then add

30 grs. red prussiate of ammonia	3lbs.

Red Prussiate of Ammonia (Ferriprussiate).

Dissolve

10 grs. sulphate of ammonia	1lb.

in

15 grs. boiling water	1½lbs.

then add this to the solution of

30 grs. red prussiate of potash	3lbs.
55 grs. boiling water	5½lbs.

Leave to rest for two days, separate from the crystallised sulphate of potash, and use the clear liquor. Instead of the ferricyanide of ammonia some printers employ the corresponding ferrocyanide, and in some cases the common yellow prussiate is used, in some instances also the expensive barium chlorate is substituted by the cheaper potassium or sodium salts, but the resulting black is not so perfect. In many instances printers prefer to use a mixture of ferro and ferricyanide.

Steam Aniline Black with insoluble chromates (Schmidlin's method.)

100 grs. water	1 gal.
12 to 15 grs. starch	1¼ to 1½lbs.

Boil, and when cooled down to about 120° F., add

20 grs. aniline salt	2lbs.
20 grs. sal-ammoniac	2lbs.

and when cold add further

5 grs. chlorate of soda powder	½lb.

stir until dissolved, and before printing add

20 grs. chromate of lead	2lbs.

(Chrome yellow pigment in paste form.)

print, dry, steam five minutes, then wash and soap in the usual way.

This colour gives a very intense black, and it may be reduced by means of thickening, in fact, with a good aniline salt 10grs. to 100, or 1lb. aniline salt to 1 gallon of thickened colour, will still give a good black, but on the small scale in the laboratory, as a rule, a stronger colour is taken in order to obtain good results.

Many methods and processes have been tried and recommended—and even patented—for developing aniline blacks by printing; however, the above described are those which have found the most extensive employment in practice.*

Great difficulties were at first experienced with the printing of aniline blacks, the colour either being liable to turn greenish by exposure, owing to the effect of sulphurous acid, or on account of the danger of rotting the fibre. These difficulties, however, are not now so much encountered, so that with a better knowledge of the aniline oils or salts most suitable for the production of good blacks, and with the use of improved steam agers or other ageing machines, the question of the production of aniline black in printing is much better understood.

In conducting small laboratory experiments where no steam is at hand, and where, therefore, a proper ageing cannot be employed, the method of developing the black is simply after printing and drying to expose the cloth, wrapped up in the neck of a flask in which water is very briskly boiled, to the action of the steam for two to five minutes, and good blacks can still be produced this way without affecting the strength of the fibre. Any of the methods above described may be used in testing one aniline salt against the other, those most useful being the ones with vanadium, with sulphide of copper paste, or with chrome yellow paste, all of which can be developed

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* I am obliged to Dr. Dreyfus, of the Clayton Aniline Company, for some useful information concerning Aniline Black, and for presents, on different occasions, of their excellent products of Aniline Oils and Salts, with which the trials of the above recipes have been made.

by a short steaming in the neck of a flask. It is also advisable to expose the printed patterns to air for some time before soaping, unless the result requires to be hurried, in which case the steaming is continued one or two minutes longer, and then the soaping is at once proceeded with.

In the thickening of aniline black colours dextrin is very often employed, since colours so thickened are not so apt to attack the cloth as strongly as if starch only has been used. This is very probably due to the fact that dextrin thickening allows the colour to remain more on the surface, and is also very probably due to the reducing action asserted by dextrin. A curious fact connected with the formation of aniline black is, that it can be developed by means of chlorate of alumina by the aid of a short steaming, and without the aid of a metallic oxidiser or oxygen carrier. Repeated trials have been made to utilise other anilines for the production of fast oxidation colours in the same way as for aniline black, but so far only one or two products have been found of any real utility, and are only sparingly employed, although it would appear from recent researches that some other anilines will be employed for the purpose at some future time. Among others the browns or bronzes obtained with phenylendiamine will no doubt be found useful if printers get over a few slight difficulties which are still in the way. The following recipe may be taken as an example for the production of a fast brown:—

Phenylen Diamine Brown.

In

100 grs, hot starch thickening .... 1 gal.

dissolve

10 grs. hydrochlorate of phenylen diamine (in powder). 1lb.

when cold add

5 grs. chlorate of soda .... ½ gal.

stir until dissolved.

Print, dry, steam lightly, or age as for aniline black, wash and soap in the usual way. The brown so produced is very strong and exceedingly fast; in connection with alizarin red it will no doubt be found useful in printing. The metallic fixers for aniline black might also be employed with brown, but as a rule they can be dispensed with, especially if the colour be developed by a short steaming. The great drawback connected with the application of this product is that the colour gets very quickly oxidised.

The author has given a great deal of attention to the production of fast browns or bronzes by this method, both by dyeing and printing, his first trials dating from 1878.

Naphthylamine Puce.

To	
100 grs. lukewarm starch paste (12 per cent.)	1gal.
add	
30 grs. nitrate of naphthylamine	3lbs.
previously mixed with	
25 grs. acetic acid	2½lbs.
stir until dissolved, then add solution of	
5 grs. chlorate of soda	½lb.
20 grs. water	2lbs.
just before printing add	
5 grs. vanadium solution	½lb.

or the corresponding amount of sulphide of copper paste in the colours then developed, in the same way as for aniline black. By reducing this colour with more thickening very fast grey shades are obtained; these can be modified by the addition of some aniline grey colour, which is itself a reduced aniline black. Phenylen diamine brown colours when reduced with thickening give a variety of very fast drabs.

Persulphocyanogen Yellow (Canarin).

This colour has not yet found the application in printworks which might have been expected, although the shade produced is a very fast one.

The first recipe, as recommended by Schmid, is about the following:—

Dissolve

I.	790 grs. chlorate of barium	79lbs.
	800 grs. boiling water	8 gals.

Dissolve

II.	520 grs. sulphate of alumina	52lbs.
	550 grs. boiling water	5½ gals.

Mix I. and II. together, stir and leave to settle; when cold, filter the chlorate of alumina formed, and make up to 36° Tw.

Yellow Colour.

250 grs. starch paste	25lbs.
5 to 10 grs. vanadium solution as below	½ to 1lb.
100 grs. sulphocyanide of alumina crystals	10 lbs.
100 grs. chlorate of alumina, 36° Tw.	10lbs.

Vanadium Solution.

20 grs. vanadiate of ammonia	2oz.
100 grs. hydrochloric acid	10oz.
200 grs. water	20oz.

boil, then add

30 cc. bisulphite of soda solution	3oz.

heat until a blue colouration is formed, then dilute to

20 litres with water	12 gals.

The colour is printed and dried, then developed in the same way as aniline black, by a passage through the steam ager. Instead of the crystallised sulphocyanide of alumina a strong solution of the salt may be used.

A modification of this colour is the following:—

Canarin Yellow.—No. 2.

In 100 grs. starch paste, 10 per cent.

dissolve, cold

40 grs. crystallised sulphocyanide of ammonia

then add

35 grs. chlorate of alumina, 36° Tw.

Print, dry, and age or steam slightly, then leave to air before washing and soaping.

Of other oxidation colours may be mentioned iron buff, obtained from the printing of acetate of iron, which, by the ageing process, gives up acetic acid, and is then oxidised from a protoxide to peroxide, but the method of fixation of this has already been mentioned.

Aniline black is very often connected with steam alizarin red; the alumina-alizarin and the black colour are printed at the same time on a two roller printing machine, the cloth dried, passed through a box containing ammonia vapour, and steamed.

The ammonia is found necessary in this case to neutralize any free acid of the aniline black colour, before steaming, otherwise a rottening of the cloth would take place. With aniline black or phenylen diamine brown, and dyed alizarin red, good effects can be produced.

Aniline black is often printed on pieces of plain dyed turkey red, or alizarin red, and very good effects have been produced by printing aniline black stripes, or other patterns on pieces dyed with the azo derivatives lately introduced in practice, such as congo and benzopurpurine reds, chrysamine yellow, azo blues, &c.

There is no doubt that the oxidation colours are of great importance in calico printing, and that they are also capable of more extensive application. Methods have been tried to produce colours on calico, which had been previously prepared with bichromate of soda or potash, dried and then printed on with aniline salt, along with a chlorate, and thus black on yellow ground is produced, if the pieces are afterwards passed through a lead salt bath, but this process is only capable of limited employment.

Catechu, of course, is also an oxidation colour, although now it is not very often used in this capacity, but formerly it was principally developed on cloth by oxidation, by means of a copper salt as, for instance:

Catechu Brown.

100 grs. cutch	10lbs.
200 grs. acetic acid	2 gals.
12 grs. sal ammoniac	1¼lb.
2 grs. verdigris	3oz.
200 gum water, 70 per cent	2 gals.

After printing, the goods are aged, and then passed through milk of lime and washed.

Among oxidation colours could also be mentioned all those which are fixed by a passage through a bichromate bath; when an oxidising reaction is produced. In fact, a group of colours can be printed, which stand this treatment and form in themselves a style—the chromed colours.

Catechu, logwood black, and Prussian blue are the principal colours of this class, and with these may be connected chrome yellow, and a few others which are either developed or not affected by the chromate bath. These chromed colours were more largely used formerly than they are now.

COLOURS FIXED BY REDUCTION.

DIRECT INDIGO PRINTING.

Glucose Process.

10 grs. indigo .... 1lb.

are ground very finely in a mortar, then a very little water is added, in order to form a paste, and the grinding is continued until the indigo is made into a very fine state of division; then more water is added to make up

50 cc. in all .... 5lbs.

after mixing well

30 grs. of Greenbank caustic soda .... 3lbs.

is dissolved in the powdered caustic soda by adding it in small portions at a time in order to prevent overheating. In fact, it is advisable to place the vessel in water in order to effect a cooling.

This caustic soda and indigo paste will keep in well stoppered bottles or closed vessels to prevent the NaOH being converted into the carbonate.

Printing Colour—(Dark Blue).

50 grs. indigo and caustic paste	5lbs.
30 to 40 grs. starch thickening	3 to 4lbs.

Starch Thickening.

100 grs. water	1 gal.
12 grs. starch	$1\frac{1}{4}$lbs.
20 grs. light British gum	2lbs.

boil and cool. For lighter blues more thickening is used.

Print on cloth prepared with glucose solution of about 10 to 12° Tw. and dry. After printing, dry at once pretty sharply, but not too hot, and steam immediately on a flask for half a minute, then air or wash with cold water.

If the reduction of indigo is successfully accomplished during the steaming, the colour obtained will be of a brownish olive cast, and it will be shown at once during the washing in cold water, when the colour on the cloth will change from olive into green, and then into blue, if, during the washing it is exposed to air to reoxidise the indigo.

After a thorough wash the cloth can be dried, but if a brighter shade is wanted, it is boiled for a few minutes with a weak caustic soda solution, which, by dissolving some greyish substance formed during the process, will leave a brighter blue on the cloth.

D. R. Bourcart, in a lecture before the Society of Chemical Industry, in 1883, gave a very interesting account of the glucose process, from which some of the following particulars have been obtained, including the illustrations of machinery and apparatus.

The proportions recommended by Messrs. Schlieper and Baum, who have been the first to introduce successfully the working of this process on a large scale, are about the following:

Standard Indigo Paste.

25 grs. indigo .... 25lbs.

are first ground to a fine powder in the dry mill, then mixed with 50 to 70 parts of water, and ground again for two days in the wet mill, enough water is then added to make in all

100 cc. water .... 10 gals.

The whole is brought into an iron vessel, to which is added

50 cc. caustic soda lye .... 5 gals.

and afterwards

58½ grs. caustic soda, 90 per cent .... 58½lbs.

the latter in medium sized lumps, the whole being stirred with an iron rod, taking care that the temperature does not raise over 40° C.; this can be prevented by placing the mixing vessel, if necessary, in another filled with cold water.

This standard paste can be readily kept in a closed iron vessel for any length of time without spoiling.

Printing Colour.

30 grs. light British gum .... 3lbs.
15 grs. Indian corn starch .... 1½lbs.
37½ grs. water .... 3¾lbs.

mix well together, then add in small quantities at a time

190 grs. caustic soda lye, at 70° Tw. .... 19lbs.

stir occasionally after each addition of caustic soda, and finally add

270 grs. standard indigo paste .... 27lbs.

and the colour is ready.

The following will give an idea of the different shades produced:

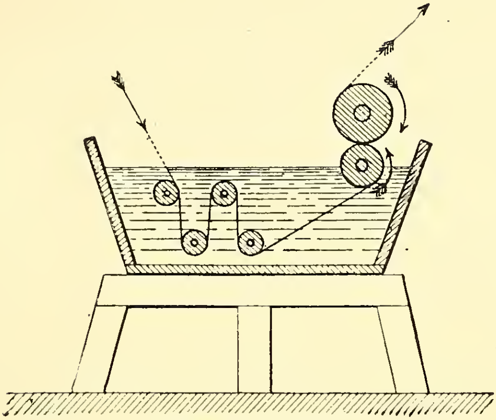
	DARK BLUE.	MEDIUM BLUE.	LIGHT BLUE.
Light calcined starch ...	3 parts	3 parts	3 parts
Indian corn ,, ...	1½ ,,	1½ ,,	1½ ,,
Water	3¾ ,,	3¾ ,,	3¾ ,,
Caustic soda lye, 70° Tw.	16 ,,	28 ,,	40 ,,
Indigo paste	30 ,,	18 ,,	6 ,,

In all cases the water, the calcined, and Indian corn starch are first mixed together, then the caustic soda lye is stirred in small portions at the time, so that it takes about 1½ to 2 hours, until all the caustic has been added, and the colour is then ready for printing.

In some instances it is recommended to heat the colour on the water bath to about 60° C. and then cool it quickly again before printing.

Preparing Cloth with Glucose.

The cloth is treated on the preparing or padding machine with a glucose (grape sugar) solution showing about 10 to 12° Tw.



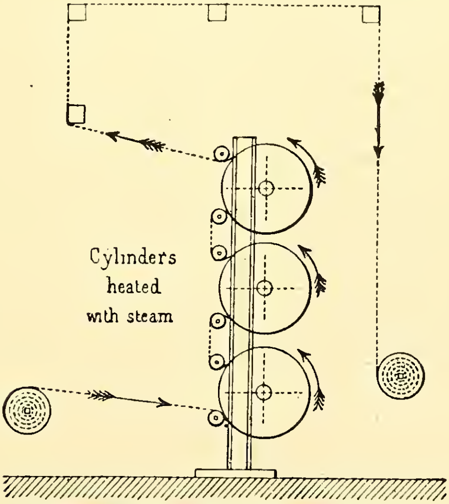
Padding machine

FIG. 5.

and containing about

250 grs. glucose	$2\frac{1}{2}$lbs.
in 1 litre water	1 gal.

It is then dried on a set of cylinders as shown in Fig. 6.



Machine for drying cloth a second time before printing

FIG. 6.

In printing, the colour, which is rather thick, must be stirred repeatedly in the colour box, also precaution is taken not to put too much pressure on the printing roller, in order that the colour remains as much as possible on the surface.

After printing the cloth is dried at once, at about 140 to 160°F., (60 to 70 C.), but not too sharply.

The drying is performed in this case by means of hot air supplied by a Roots blower (Fig. 7 and Fig. 8.)

The reason why the cloth must be treated at once is, that if exposed to air the printed colour on the cloth will attract carbonic acid, which, by converting the caustic into carbonate of soda, will render the colour almost useless.

The steaming is for this reason immediately proceeded with, and is effected in a specially constructed apparatus (Fig. 9), in which is maintained a constant supply of wet steam, by allowing the steam to pass through the water contained in a reservoir, at the bottom of the steaming chamber. The steam must also be free from air, or else the reduction will be to a certain extent prevented.

Cloth is passed in full width through this steaming chest, in which it is only exposed for about 20 seconds, this time being quite sufficient to effect a reduction.

A modification of Mather and Platt's steam ager is also employed sometimes for this steaming process.

Fig. 10 shows the connection of the different arrangements for printing, drying, and steaming of the cloth printed with the indigo colour.

The washing must be effected with a large quantity of water, in order to remove rapidly the caustic soda; by arranging the washing properly the colour will not run, but if the washing is effected slowly the colour is very liable to run and will tinge the white.

The operation is performed on a machine consisting of a series of cisterns, as in the dunging process (Fig. 11.)

This indigo blue is now very largely printed on red dyed cloth, and effects are produced of indigo blue stripes, or

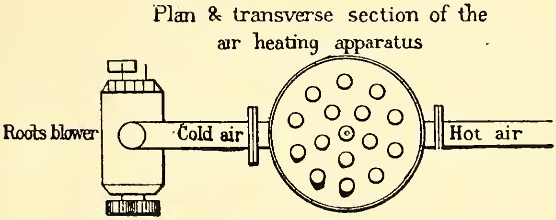


FIG. 7.

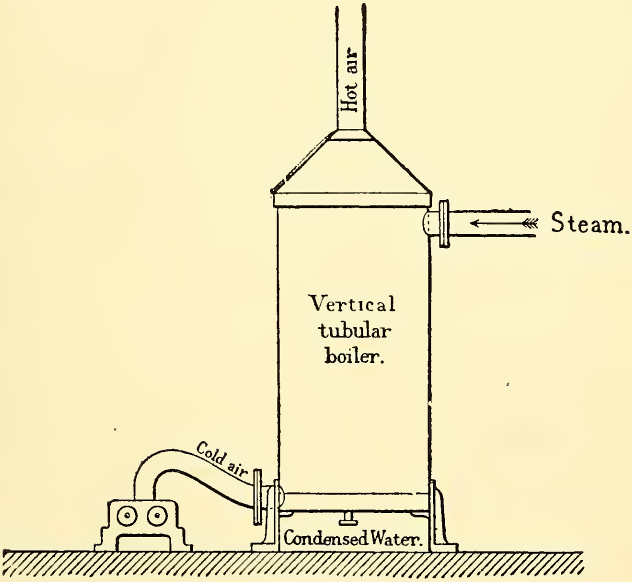


FIG. 8.

other patterns on red ground. The cloth is, of course, dyed plain alizarin red beforehand in the usual way, and then the blue is printed on the dry red cloth, which must be prepared with hot glucose solution before printing.

The indigo blue thus printed effects a discharge of the red and the fixing of the blue at the same time, but very often it is not aimed at producing the discharge, but simply to superpose the blue on the red.

Blue is often printed on cloth mordanted with alumina.

and the red dyed afterwards, but in this case the steaming and soaping required to effect the brightening of the red will, to a certain extent impoverish the blue, so that the first method is after all preferable, although a little more expensive, owing to the larger amount of alizarin used.

In printing the indigo blue on the turkey red cloth, the steaming is effected as before, in the special steam chest, then the cloth is well washed and passed in a continuous manner through weak sulphuric acid at 10° Tw., for 10 to 15 seconds, then immediately through water to wash off the acid, then through soda solution at about 3° Tw. and washed. Finally the cloth is soaped at the boil and dried. To stand the action of the acid bath in mordanting the cloth for turkey red a certain amount of lime is fixed on the fibre, according to Schlieper and Baum, as aluminate of soda.

TURKEY RED ON CLOTH WHICH IS PRINTED AFTERWARDS WITH INDIGO.

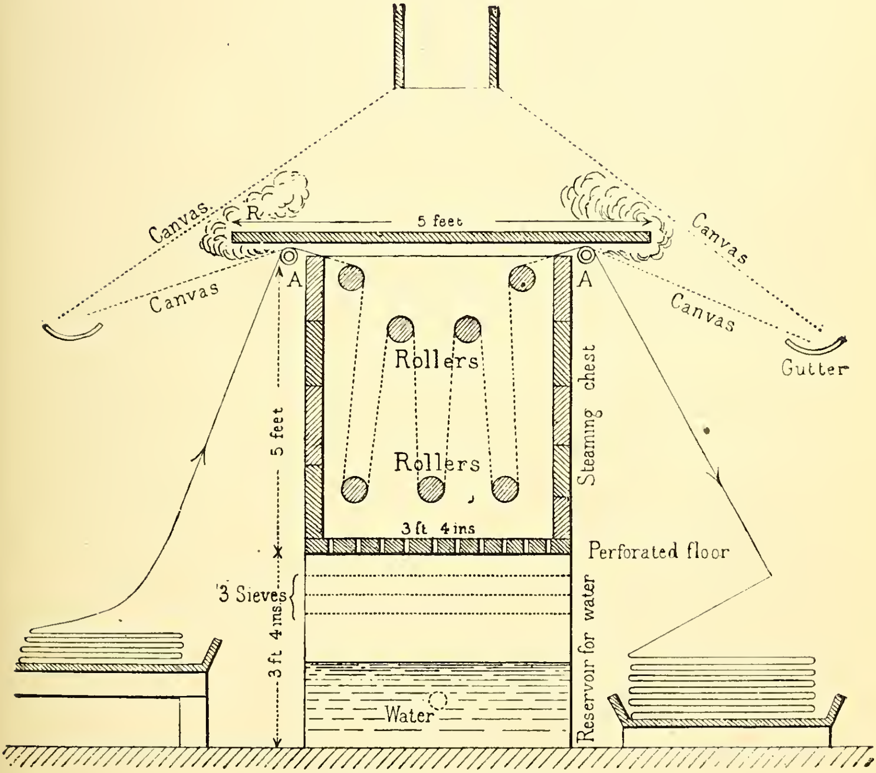
In 125 cc. caustic soda lye of about 52° Tw. ..... 1¼ gals.
dissolve
20 grs. dry alumina .... 2lbs.
by heating for two or three hours or more; then dilute to make up in all
500 cc. liquor .... 5 gals.
neutralised by
25 cc. hydrochloric acid (1.15 sp. gr.)............ 2½ lbs.
and make up with water to
1 litre in all.. 10 gals.

The caustic lye used above must correspond to an equal volume of the hydrochloric acid.

In preparing the cloth take

5 parts of this mordant to 1 to 2 parts of water.

Pad the cloth in this mordant, dry on the cylinder, then pass through ageing machine, put cloth up in bundles, and allow it to lay overnight, or even for a day or two. Then put through the dunging machine for half-an-hour with a



Apparatus for steaming the indigo

FIG. 9.

strong chalk bath, wash slightly, put cloth in bundles for 24 hours, and repeat the passage through chalk, when, according to the inventors of this process, aluminate of lime is found on the fibre; wash and leave standing again for 24 hours, then wash well, and the cloth is ready for dyeing.

The process of dyeing with alizarin is also very interesting. The dyeing is effected in large becks, about 5 yards long, 1½ yards deep, and 2 yards wide, the cloth being passed in full width on a system of rollers as on the dunging machines.

The bath is prepared as follows:—For every

1 litre water	100 gals.
¾ grs. 20 per cent. alizarin	¾lb.
6 grs. clear lime water	6lbs.

During the dyeing operation the same quantity of lime water and the corresponding amount of alizarin are added to replace what has been taken up by the pieces in the formation of the red.

The bath is kept at a temperature of 90 to 95° C, and the cloth takes 3 to 3½ minutes in passing through the dyebath; this, therefore, is a much quicker method than the one generally followed.

For dark reds the dyeing is repeated, but after the first dyeing the cloth is brightened.

The Brightening Process

is performed as follows:—The cloth is treated with a so-called *acid soap*, which is obtained by first preparing a soap with *ricinus* or castor oil and caustic soda, and then neutralising the half of the caustic employed by means of hydrochloric acid. The acid soap collects at the top, and can be used in the treatment of the dyed cloth. After drying, the cloth is steamed for one hour, for which, if red alone, pressure can be employed, but if red and blue, without pressure. A soaping, of course, will follow the end of the brightening process.

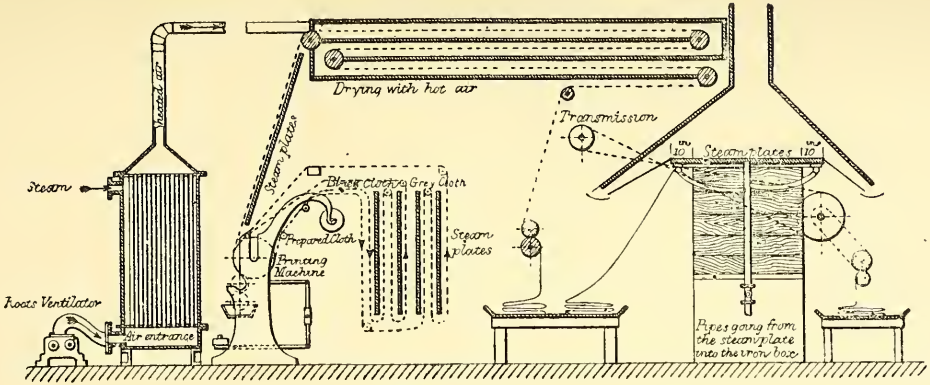
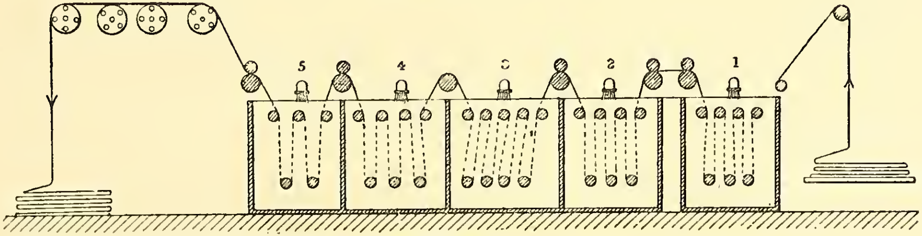


Fig. 10.



Large fly dung-beck for the washing of printed pieces

Fig. 11.

This method has been introduced in practice by Messrs. Schlieper and Baum in connection with the glucose indigo printing process.

RESIST OR RESERVE

under indigo blue (glucose process).

White Reserve.

1 litre thickening (calcined starch)	1 gal.
150 grs. precipitated sulphur	1½lbs.

The sulphur must be free from grit, and ground on a mill before use.

Yellow Reserve.

1 litre thickening	1 gal.
200 grs. cadmium chloride	2lbs.
150 grs. precipitated sulphur	1½lbs.

Red Reserve.

1 litre acetate of alumina	1 gal.
10 grs. tin crystals	1½oz.
150 grs. precipitated sulphur	1½lbs.
800 grs. dextrine	8lbs.

Resist for Light Blue (under dark blue).

1 litre caustic soda 50° Tw.	1 gal.
400 grs. dextrin	4lbs.
100 grs. Indian corn starch.	1lb.

Boil, stir until cold.

All these resists are printed on material previously prepared in glucose, and the indigo colour is then printed or padded on. The caustic soda, in destroying the glucose partially, allows a weaker blue to be produced. For the red resist the process is continued as follows:—Print and dry, and after steaming for reducing the indigo, pass into the dunging cistern containing weak arseniate of soda and sal ammoniac; the cloth must be passed in a continuous manner, and the bath strengthened with both arseniate and sal ammoniac to replace the salts decomposed or taken up by the pieces in passing through. If the bath smells too strongly of ammonia it is neutralised by means of hydrochloric acid.

If little blue and much red is in the pattern, then a bath of silicate of soda of about 3° Tw. and cow-dung can be used instead. After the dunging and a good wash, the dyeing with alizarin follows, as mentioned before.

Red and Blue (by glucose process).

Print indigo caustic soda paste and a thickened aluminate of soda on two separate rollers at the same time, on cloth previously prepared with glucose. After drying, steam for the reduction of indigo, then pass through bath with sal ammoniac to fix the alumina, wash well, and then dye in alizarin, following the process of dyeing by brightening as before.

Direct Alizarin Red and Indigo Blue.

The author has made many experiments on the method for fixing red and blue at the same time by a direct process without the necessity of passing through the dyeing operation with alizarin, in order to see if other colours could not be produced at the same time. After many trials, a red has been obtained by a new method, which might find employment in calico printing along with indigo blue or for other purposes. The process is as follows:—

Direct Alkaline Red with Alizarin.

80 grs. starch paste 10 per cent....	8lbs.
60 grs. alizarin 20 per cent............................	6lbs.
60 grs. caustic soda lye...................................	6lbs.
1 dry $\mathrm{Na\,OH}$ 98° per cent. 1 water.	
100 grs. aluminate of soda solution	1 gal.

The blue is prepared by the well known glucose method, adding, however, the glucose to the colour.

Indigo Blue.

I.	15 grs. indigo finely ground	1½lbs.
	40 grs. water	4lbs.
	30 grs. caustic soda powder (98 per cent.)	3lbs.
II.	30 grs. glucose	3lbs.
	20 grs. dextrine	2lbs.
	50 to 60 cc. water	5 to 6lbs.
	Are heated on the water bath, and, after dissolving, well cooled.	

When thoroughly cold, mix I. and II. in a vessel immersed in water to effect a cooling.

The red and blue are printed at the same time on unprepared cloth, dried immediately, and steamed as for indigo; they are then either aged or exposed to air, or washed at once. If the proportions of the red colour are right, and the pattern on the roller is deeply engraved, a good red will ultimately be obtained by taking the precaution to wash the cloth with a large quantity of running water, which will remove the caustic soda, and will leave behind sufficient colour to give a good red.

A bath with sal ammoniac and arseniate of soda acts in some cases beneficially for the fixation of this red, but if, as I have said before, the proportions have been well arranged, no such bath will be required. The red thus formed must be brightened by an oiling, steaming, and soaping in the usual way. If after washing and before oiling the cloth is passed in a warm weak bath of alizarin oil, the red will be better fixed, and in fact a fair red can even be obtained by boiling at once in an alizarin oil or oleine bath, and then soaping without steaming.

The difficulty connected with this new method of fixing alizarin red in printing along with indigo is that the latter is apt to become weakened by the oiling and soaping; but this difficulty is also encountered when producing the red along with the blue by the Schlieper's methods.

I have also fixed the red and obtained even a fair colour by printing on glucose prepared cloth, thus making it possible to use the glucose process in the usual way.

I have found that a very simple way of preparing the alkaline alizarin red for printing is simply to mix some caustic soda lye to an ordinary steam alizarin red colour, which is made a little stronger for the purpose, that the soda lye will not dilute it too much. In this case, however, the bath of binarseniate and of sal ammoniac will be necessary for fixing the alumina on the fibre.

I call the attention of printers and chemists to this alkaline method of fixation of alizarin red, because it can be applied also for other colours, or at all events for other alizarin shades; for instance, by using the iron or the chromium alkaline mordant, alizarin can be fixed on the fibre by the same method, and in this way all the shades of the madder styles, viz., reds, pinks, browns, purples, chocolates, &c., could be produced and connected with indigo; and even a yellow from cadmium or perhaps lead, without mentioning buff, which could be so readily produced by a simple alkaline iron colour.

REDUCED INDIGO PRINTING.

The production of the so-called China blue by printing a reduced indigo colour, has lost much of its importance since the introduction of the glucose process, the more so as by the China blue method only light shades can be produced. These shades are, however, brighter than those generally obtained by means of the glucose method, but by proper management very good light blues are also obtained by the latter precess. As a rule a colour is printed, consisting of reduced indigo, properly thickened with gum, and the print is then allowed to air, when the indigo white is oxidized to indigo blue, and thus permanently fixed on the fibre. The best reduced indigo is the one obtained by the hydrosulphite process of Schützemberger and De Lalande, and which is found in commerce already prepared for printing.

The following recipe will give an idea how the blue can be produced:—

Blue with Reduced Indigo.

10 grs. indigo .... 10lbs.
are ground in water, and then enough of the latter is added to make up to
70 grs. water in all.................................. 1 gal.
heat, then dissolve in
7½ to 10 grs. ground gum senegal...............7¼ to 10lbs.
then add
15 grs. saturated hydrosulphite .... 1½ gal.
1½ grs. milk of lime (20 per cent. CaO) ...... 1lb. 4 oz.
heat 20 minutes to about 60° C., then cool to about 30° and add
5 grs. hydrosulphite .... ½ gal.
1½ grs. milk of lime .... 1lbs. 4oz.
the colour is allowed to stand for some time in order to effect a complete reduction, then it is heated on a water bath at about 30° C. before printing.

After printing, the pieces are aired for 24 hours, to effect the reoxidation of indigo white into the blue, and, if necessary, can be passed into a chrome bath, then washed, soaped, and dried.

Under the name of *Pencil Blue* an indigo preparation has been a long time in use, consisting of ground indigo, caustic soda, or potash and orpiment, when indigotin is speedily reduced to the indigo white, and can be printed on the cloth, but the result is not always satisfactory, owing to the avidity of the indigo white for oxygen, and conversion into the blue; but the method has been long in use among the eastern nations, for applying reduced indigo on the fibre by means of the pencil.

Another method of fixation of indigo on the fibre by direct printing, consists in printing a colour prepared with ground indigo, acetate of iron, ferrous sulphate and gum senegal solution, and after printing and resting for some time the cloth is worked in six baths containing: the two first, lime; the third, copperas; the fourth, caustic soda; the fifth, weak sulphuric acid; and the last, fresh water. The method is therefore rather tedious, and seldom, if at all, employed, as the cost is pretty high. Indigo can be printed also by a direct method, by preparing a colour containing caustic soda, indigo and red phosphorus, and steaming, as by the glucose process, when deep blues are produced.

A more practical process consists in printing on indigo reduced by means of a proto compound of tin, as by the following recipe:—

Blue with Reduced Indigo.—No. 2.

10 grs. ground indigo	5lbs.
10 grs. granulated tin	5lbs.
50 cc. water	2½ gals.
12 cc. caustic soda lye, 68° Tw.	2½ quarts.

boil 1½ hours, pass through a sieve, and wash with

10 cc. water	½ gal.

which add to the rest, then add further

12 cc. protochloride of tin solution, 120$_0$ Tw.	2½ quarts.
7 cc. lime juice, 20° Tw.	1½ ,,
60 grs. gum water	3 gals.

Pass through a sieve, grind well for two days, then strain and print.

This blue is raised in an alkaline bath, for which principally milk of lime is employed, then the pieces are washed and afterwards passed through weak acid and washed, soaped and dried.

ARTIFICIAL INDIGO

(*Nitro Phenyl Propiolic Acid.*)

This is only sparingly used on account of its high price, especially since the introduction of the glucose process o direct indigo printing, It is now only seldom employed for patterns where much white and little colour is required.

Propiolic Acid—Standard.

10 grs. starch	1lb.
100 grs. water	1 gal.

are boiled, and while still hot

15 grs. borax	1½lbs.

are dissolved in, when cold,

90 grs. propiolic acid, 20 per cent. paste	9lbs.

are added: before printing

10 grs. xantate of soda	1lb.

are dissolved in, and the colour is tinted with aniline blue. For lighter shade this colour is reduced by means of starch paste.

Print, dry, hang for 12 to 24 hours in a room heated to 25° C. to develop the blue, then pass through soda solution, wash and soap.

This blue can be resisted as follows:

White Resist under Artificial Indigo.

100 grs. lime juice, 40° Tw	1 gal.
25 grs. caustic soda, 50° Tw	¼ gal.
2 grs. oil	3oz.
40 grs. dextrine	4lbs.
1¼ grs. oxalic acid	1½ oz.

Print, dry, and then print or pad the blue on.

The propiolic acid colours can be printed at the same time with mordants for alizarin reds, and thus produce patterns of red and blue on white ground; in this case, after printing, the goods are aged, dunged at 55° C. in binarseniate of soda, and dyed with alizarin, in the usual way, and soaped at a temperature not higher than 75° C.

Not only white but coloured resists can be printed under the propiolic acid, and not only reds but chrome yellows and orange can be produced. A variety of patterns can be obtained by the propiolic acid connected with other colours. Xantate of soda imparts to the goods a peculiar smell, which is decidedly a drawback; to do away with this the goods can be passed for two minutes through the Mather and Platt steam ager.

INDOPHENOL BLUE.

If not equal to indigo in fastness, is analogous to it on account of its method of fixation, which is also effected by a reduction process. This blue deserves more attention than it has had, since it might be found capable of many useful employments, one of which has been successfully effected by Mr. Horace Koechlin, to whom is due the discovery of this colouring matter. Mr. Koechlin applies the indophenol blue on wool cloth, previously dyed with a xilidin or any other azo scarlet, and thus obtains patterns of blue and red similar to those produced on cotton by the glucose indigo process.

He applies also the indophenol blue on cotton cloth previously dyed with benzopurpurin, and thus obtains patterns of blue on red ground.

The following details have been kindly supplied to me by the above gentleman, along with the patterns of red and blue on cotton, as shown among the printed patterns.

Dye in benzopurpurin in the usual way and dry. Print the following:—

Indophenol Blue.

75 grs. indophenol powder	1½lbs.
½ litre acetic acid	1 gal.
½ litre acetate of tin, 30° Tw	1 gal.
400 grs. gum	8 lbs.

Leave over night in order to reduce the indophenol blue to white, heat to 40° C. for half an hour.

Print, dry, steam one hour, then pass through bichromate of potash bath at 10 grs. per litre, or 1½ oz. per gal. at 20° C.; wash, then soap for 20 minutes at 20° C., wash and dry.

The indophenol comes in commerce already reduced in the form of white paste, and its method of application is as follows.

Indophenol Blue.—No. 2.

Light shade.

100 grs. gum water	1 gal.
20 grs. indophenol white paste	2lbs.

Mix, print on oleine prepared cloth, steam one hour, pass two minutes through bichromate solution at 55° C., wash, soap slightly and dry.

For dark blue take

75 grs. reduced indophenol paste	3 gals.
25 grs. gum water	1 gal.

Print, dry, steam and pass through bichrome or bleaching liquor.

Before leaving this chapter I must express my thanks to the Greenbank Alkali Co., and especially to Mr. Menzies, for a present of their caustic soda powder, with which all the experiments on the glucose indigo printing process have been made by myself or my pupils.

DYED COLOURS.

All dyestuffs capable of being fixed on cotton cloth by means of mordants can be employed for dyeing cloth on which the mordants have been printed, and this plan is sometimes followed, but not so much since the development of steam colours. For instance, the dyewoods can be dyed on printed colours, and are very often used for the purpose, in connection with alizarin, for the production of compound shades, and in some cases for black patterns on white grounds, but their use is not a very extensive one. Aniline colours are also used sometimes by this method; but alizarin finds the most important application in the dyeing upon printed mordants, forming in fact the alizarin dyed style also known as Madder style.

DYED ALIZARIN COLOURS.

In this style the thickened mordants are first printed on, then dried, aged, and dunged and dyed with alizarin.

The thickened mordants are prepared in about the following manner, being the acetates of alumina or iron, or a mixture of both.

Red.—No. 1.

100 grs. acetate of alumina 9° Tw	1 gal.
12½ grs. wheat starch	1¼lbs.
12½ grs. calcined starch	1¼lbs.
5 grs. gallipoli (olive) oil	½lb.
1 gr. magenta crystals	⅛oz.

Or enough of strong magenta solution to tinge the colour.

Boil, stir until cold, then print and dry.

Red.—No. 2.

100 grs. acetate of alumina 12° Tw.	1 gal.
100 grs. water	1 gal.
25 grs. starch	2½lbs.
10 grs. calcined farina	1lb.
2½ grs. olive oil	¼lb.

This will give a lighter red than No. 1, whilst if a still lighter colour is required, more water is taken in proportion, for instance—

Light Red.—No. 3.

50 grs. acetate of alumina 12° Tw.	½ gal.
100 grs. water	1 gal.
15 grs. starch	1½lbs.
10 grs. dextrin	1lb.
2½ grs. olive oil	¼lb.

In looking over the recipes published by the different authors, it will be found that they vary sometimes considerably in the proportions employed, and especially in the strength of the acetate of alumina which is recommended.

For laboratory work it will be found necessary to prepare a stronger colour by having a stronger acetate of alumina, since if no ageing apparatus is at hand it will be found difficult to fix enough alumina mordant on the cloth to have a good red; in fact, it will be found very difficult to produce as good a red in the laboratory as in the works.

In some cases, in the preparation of the colours, a certain amount of tin is added, while for tingeing or sighting purposes besides magenta, any other red solution can be employed which would not interfere with the alumina mordant.

It may be taken as a general rule that an acetate of alumina of about 10° Tw., or varying from 8 to 12° Tw., properly thickened by dissolving in it sufficient British gum, or by boiling the same with starch, will give a fair result in the laboratory.

The addition of tin salt will greatly improve the colours obtained, and impart to them a yellow shade, the following serving as an example:

To Red No. 1 add

5 grs. tin crystals	½lb.
10 grs. acetic acid	1lb.

Oxymuriate of tin is also used for the same purpose.

By reducing the red colours, pinks and roses are produced. The reduction, or rather dilution, can be effected either by mixing any of the standard red colours with the necessary amount of thickening, or can be prepared especially for the purpose. If a bluer pink is required no tin is employed along with the acetate of alumina.

Pink or Rose.

100 cc. boiling water	1 gal.
5 cc. acetic acid	½lb.
25 cc. acetate of alumina 9° Tw.	2½lbs.
65 grs. calcined farina	6½lbs.
1 gr. olive oil	1 oz.
1 gr. turpentine	1 oz.

It is needless to say that the alumina mordant used in the preparation of those colours should be thoroughly free from iron, and this not only for the reds but especially for the pinks, which would otherwise not possess the required brightness.

Purple.—No. 1.

100 grs. boiling water	1 gal.
15 grs. acetate of iron 16° Tw	1½lbs.
75 grs. British gum	7½lbs.
1 gr. turpentine	1½ oz.

Brighter colours are obtained by the aid of arsenious acid preparations, known under the name of "purple fixing liquor."

Purple.—No. 2.

10 grs. acetate of iron 20° Tw	1lb.
20 grs. purple fixing liquor	2lbs.
100 grs. gum water (60 dark calcined farina to 100 of water, or 6lbs. per gallon)	1 gal.

Purple Fixing Liquor.

1 litre water	1 gal.
1250 grs. soda crystals	12½lbs.
1125 grs. arsenious acid	11¼lbs.

Boil until dissolved, then add at about 120 F.

25 litres pyrolignous acid	25 gals.

Leave to rest for several days, decant the clear liquor, to which add

350 grs. hydrochloric acid	3½lbs.

These purple colours can be reduced by means of thickening according to requirements; they are sometimes also spoken of as *lilacs.*

Purple.—No. 3.

100 grs. crude acetic acid 6° Tw.	1 gal.
100 grs. acetate of iron (black iron liquor) 15° Tw.	1 gal.
400 grs. fixing liquor No. 2 (as below)	4 gals.
400 grs. gum water (70 per cent., or 7lbs. dextrine per gallon	4 gals.

Fixing Liquor.—No. 2.

1 litre water	10 gals.
2 grs. lime	3¼ oz.
15 grs. white arsenic	1½lbs.
13 grs. sulphate of copper	1¼lbs.

Boil a quarter of an hour, then cool.

By mixing acetate of alumina and acetate of iron in the same colour, a great variety of shades can be produced, varying according to the proportion of either; when dyed in alizarin they produce shades generally known under the name of *chocolates* or *puce.* The following may be taken as example:—

100 grs. acetate of alumina 20° Tw.	1 gal.
30 grs. acetate of iron 20 Tw.	3lbs.
15 grs. starch	1½lbs.
1½ grs. olive oil	2½ oz.

Boil, then stir until cold.

By adding other dyestuffs to the alizarin bath, these chocolate shades can be very greatly varied.

Brown.

In 1,000 grs. water	1 gal.

Boil for six hours,

400 grs. catechu	4lbs.

then add

100 grs. acetic acid	1lb.

and enough water to make up to

1,000 grs.	1 gal.

leave to stand two days, then decant, heat to 130° F., and add

200 grs. sal ammoniac.	2lbs.

when dissolved thicken with gum senegal in proportion of

400 grs. per litre, or	4lbs. per gal.

The colour is then prepared with

100 grs. brown standard	1 gal.
12½ grs. acetate of copper 16° Tw.	1¼lbs.

Acetate of Copper.

In

1,000 grs. hot water	1 gal.

dissolve

400 grs. lead acetate	4lbs.
400 grs. sulphate of copper	4lbs.

Leave to settle, filter, and dilute to 16° Tw.

Black

Is now very little if at all used, having been superseded by aniline black.

100 grs. water	1 gal.
100 grs. black iron liquor (acetate of iron) 40° Tw.	1 gal.
25 grs. starch or flour	2½lbs.
10 grs. quercitron liquor 25° Tw.	1lb.
10 grs. logwood extract 25° Tw.	1lb.
2 grs. olive oil	4 oz.

Boil in the usual way.

After the mordants have been printed, the cloth is dried, precaution being taken not to allow it to come in contact with a heated surface, which would act injuriously on the alumina mordants. Then follows the

Ageing Process.

This has the object of decomposing the acetates, so that the acetic acid is driven off and a basic insoluble product is deposited on the fibre. For this the ageing machines are still employed, but the newer steam ager is now successfully used, the cloth being passed very rapidly through the apparatus and exposed in the ager for about two minutes to a temperature of 185° F.

Plate VII. illustrates Mather and Platt's steam ager, which has already been mentioned in the chapter relating to aniline black.

Fig. 12 is Gadd's new steam ageing machine, for the drawing of which I am indebted to the kindness of that firm.

The cloth is then folded up and laid down in bundles over night. The decomposition of the mordants, which was started by the action of the steam in the steam ager, will now slowly go on by itself.

It has been observed, however, that the mordants aged in the steam ager by the quick process do not yield as fast colours as if a slower ageing is employed.

The ageing does not effect the complete precipitation of a suitable mordant on the fibre, and must be followed by the so-called *dunging or fixing process.*

This operation consists simply in passing the cloth in a continuous manner through the dunging apparatus, or cisterns containing the dunging liquors (Plate VIII). The object of this is, first of all the complete precipitation of the insoluble compound on the fibre, and at the same time the removing of the thickening, and also any portion of the mordant which has not been fixed on the fibre. The dunging was performed formerly simply by cow dung, with or without

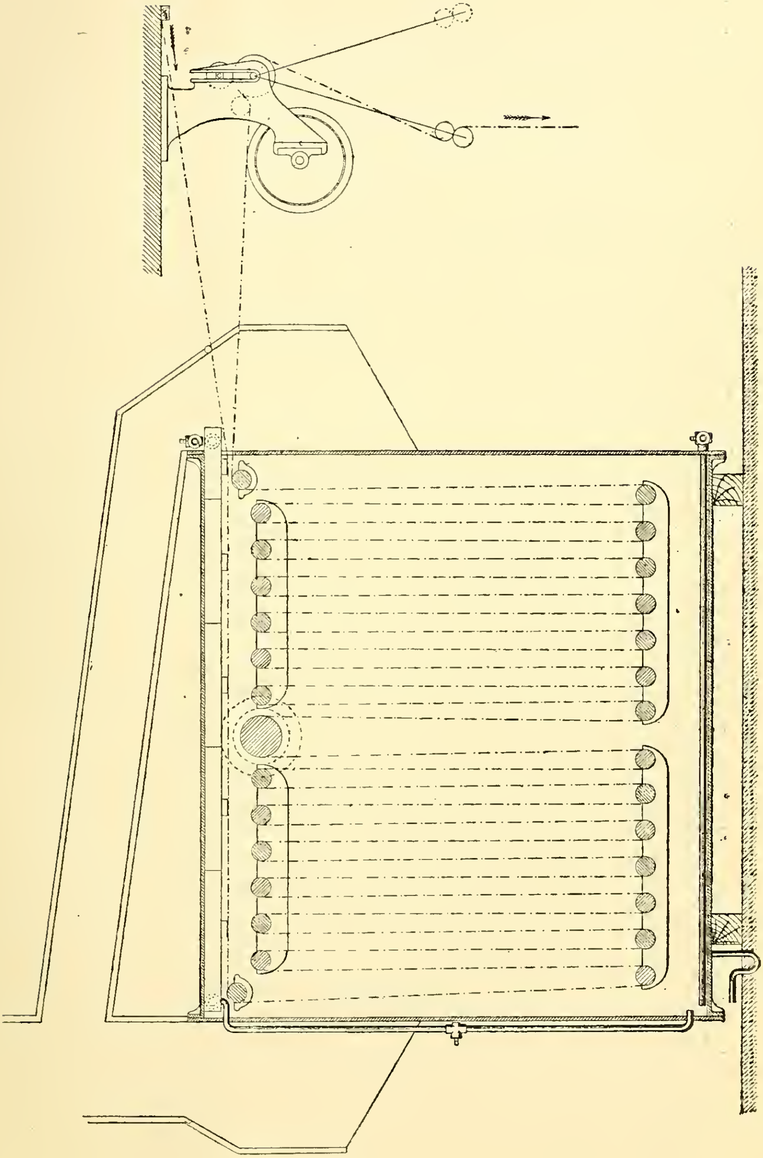


FIG. 12.

addition of chalk, but is now mostly done by substitutes, of which the principal are—

Arseniate and binarseniate of soda.
Phosphate of soda.
Silicate of soda.

The arseniate and binarseniate are the agents most employed in England, sometimes also dung and chalk and the substitutes are used at the same time.

The temperature of the bath is arranged according to the style of goods to be dunged; light colours are dunged at lower temperature, not higher than 65° C., while deeper colours require a higher temperature, but not higher than 75 or 80° C.

The pieces are passed full width through the dunging cistern, containing two to five parts cow dung for every 100 of water, and for colours containing much acid a few pounds of chalk for every cistern, and the operation lasts two or three minutes.

A second dunging follows by passing the cloth in the form of a rope through the roller squeezing machine, which is on the same principle as the alizarin dyeing machine. For the second dunging the temperature must be arranged according to the colours, but must not go higher than 75 or 76° C.

It is advisable to have, when possible, a washing between the two dunging operations, but many dyers prefer passing the pieces from the first into the second dunging without washing.

On a small scale the dunging is effected in a porcelain or earthenware vessel, in which the cloth is worked up and down through the liquor by hand. In the second dunging 20 minutes to half an hour are employed.

Cow dung gives better results than any of the substitutes, which, however, if used with judgment, leave nothing to be desired.

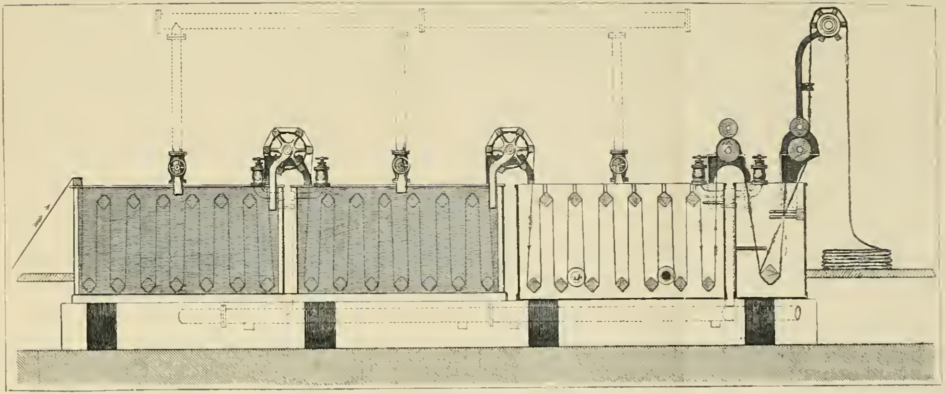


PLATE VIII.—DUNGING CISTERNS

Arseniate of Soda.

For the strongest dunging liquor use

1 gr. arseniate of soda solution 28° Tw.	1lb.
In 100 cc. water	10 gals.

For the weakest dunging bath—

1 gr. arseniate of soda solution 28° Tw.	1lb.
250 to 300 cc. water	25 to 30 gals.

The arseniate must be free from alkali, or else it will not act well, as it will dissolve the weak mordants instead of fixing them.

Binarseniate of Soda

must be rendered neutral by means of chalk or caustic soda, taking care in the latter case that no excess is used.

Silicate of Soda

is more used on the Continent than in England, and gives very good results if free from alkali.

The following proportions may be taken as examples for the dunging baths. The cloth is passed through two baths.

1*st Bath.*

1 litre water 75° C.	10 gals.
10 grs. silicate of soda 15° Tw.	1lb.
1 gr. chalk	1½oz.
5 grs. arseniate of soda 15° Tw.	½lb.

Duration, two minutes.

2*nd Bath.*

1 litre water 85° C.	10 gals.
100 grs. cow-dung	10lbs.
10 grs. chalk	1lb.
10 grs. arseniate of soda (dunging liquor) 15° Tw.	1lb.

Duration, two minutes. Wash; and then work for forty minutes with

1 litre water 85° C.	10 gals.
150 grs. cow-dung	15lbs.
15 grs. chalk	1½lbs.

The washing is now mostly effected on the washing machines, which will be mentioned and illustrated later on. After washing, the cloth is ready for

THE DYEING.

This is effected on machines constructed on a similar principle to the washing machines of the bleaching process, and will be mentioned again later on. Here will be mentioned only the preparation of the dye bath. The quantity of alizarin depends of course upon the amount of colour to be produced on the cloth; for heavy patterns containing much red the quantity may be taken in the proportion of 3 to 5 per cent. of the weight of cloth, but this is a question which can only be decided by trial, and experienced dyers will soon form an idea of the dyestuff required from the amount of red to be produced.

The following may be taken as the corresponding proportion of the different products to be employed in the dye bath.

Say for 1,000 grammes cloth, for medium pattern—

10 grs. alizarin 20 per cent	10lbs.
1 gr. tannic acid	1lb.
1 gr. glue	1lb.
5 grs. alizarin oil	5lbs.
·2 grs. chalk	2oz.

The dyeing is started at about 25° C., and brought in one hour to 72° C., where it is left for a quarter of an hour.

Some chemists add a small amount of sulphuric acid to the dyebath, with good results.

After dyeing, the cloth is washed, dried, oiled with a solution of alizarin oil at 5 per cent., dried again, and steamed for one hour. Then follows a brightening with

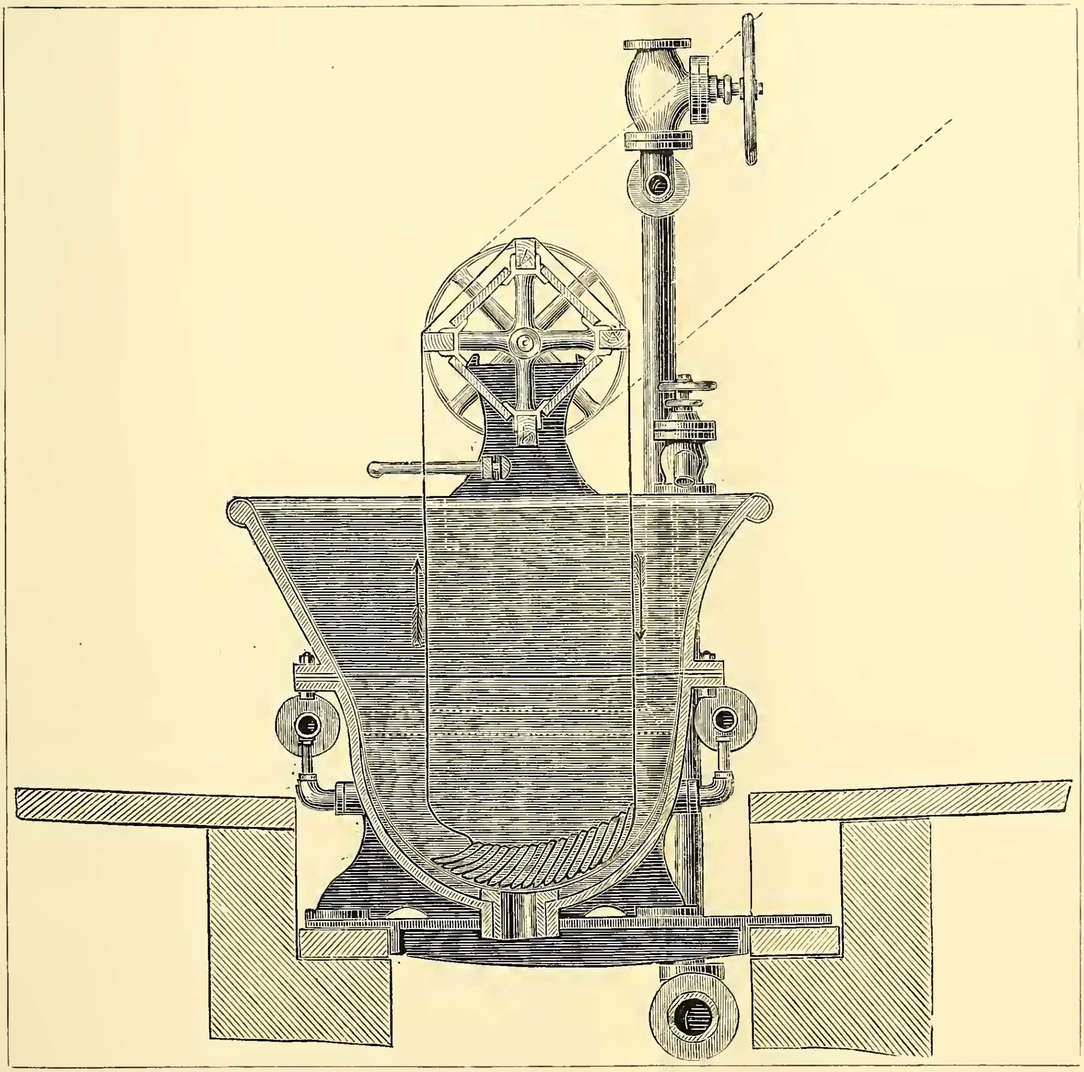


PLATE IX.—COPPER CASED DYE BECK

soap, for which the cloth is treated in two consecutive baths with about 1 to 2 per cent. of soap to the weight of cloth, at a temperature of 75° C. Some printers even soap at the boil in a continuous way in the soaping machines; some also effect the soaping in closed vessels under pressure.

The madder styles, which were at one time very largely used, have not been so much in vogue in the last few years, but prints in which dyed alizarin red enters have been, and are now, very extensively produced, especially for designs of red and aniline black on white ground.

RESISTING AND DISCHARGING PROCESSES.

To the dyed colours belong also those which have been applied by the padding process, either on the padding machine or by means of the padding roller, and which give rise to a great variety of patterns, which can be produced by the discharging or resisting method.

The so-called padding styles, in reality a modification of the madder styles or alizarin dyed colours, belong to this class, and although not so largely used as formerly, they are still employed in printworks to a certain extent. In the following chapter will be treated the most important resists and discharges, and the Turkey red, indigo, and manganese bronze styles, which will be treated separately. Although some of the resists mentioned are employed under steam or oxidation colours, they are treated here for the sake of convenience, the more so that many patterns are produced by the padding of steam or oxidation colours on resisted cloth.

In the resisting process the cloth is printed with a preparation which will prevent the colour from being fixed on the spots where the *resist* or *reserve* has been applied. These resists or reserves may act simply mechanically, such as wax or white pigments (as china clay, &c.), while others will act chemically by forming such a chemical combination with the colour or product which is afterwards applied as to prevent its fixation on the fibre.

Mechanical Resists or Reserves.

Wax is the oldest one employed for reserving colours, and is still now used in eastern countries, but very seldom in the modern industry, owing to the difficulty of applying it in a proper way and in a continuous manner on the printing machine.

The method of producing patterns on cotton cloth followed by the Hindoos is a very slow one, but at the same time the process is very clever, and not only patterns of one colour are thus produced but also patterns containing different colours and pretty intricate designs.

The white pigments are very often employed as mechanical resists, the principal ones being china clay, sulphate of lead, and barium sulphate. When applied on the machine they have a tendency to fill the engraving, and to get over this difficulty starch is recommended as a mechanical resist, being added to the printing or resisting colour in its powdered dry state.

Chemical Resists.

Reserves under alumina and iron mordants afterwards dyed in alizarin colours.

These reserves are mostly composed of citric acid and citrate of soda, which is prepared in making up the colour by mixing lime juice with soda lye; this resist, when applied on the cloth, prevents the fixation of the oxides of iron or alumina on the fibre, and therefore when the cloth is afterwards dunged and dyed in the alizarin bath the reserved spots remain white, while the colours will be formed where the mordant has been fixed; consequently not only reds and pinks can be thus reserved, but purples, chocolates, and blacks also. The reserves are prepared in about the following way:—

For Red Mordants.

Add

100 cc. gum senegal water (60 per cent.)	1 gal.

to a well stirred mixture of

100 cc. boiling water	1 gal.
140 cc. China clay	14lbs.

then add

75 ccs. lime juice 50° Tw.	¾ gal.
55 ccs. soda lye 70° Tw.	½ gal.

previously boiled. Boil the whole 20 minutes.

For Purple.

To

100 cc. gum water 6 per cent	1 gal.

stir in

120 grs. China clay	12lbs.

previously mixed with

50 grs. boiling water	½ gal.

then add a previously boiled mixture of

100 cc. lime juice 60° Tw.	1 gal.
75 cc. soda lye 70° Tw.	¾ gal.

Citric acid liquor or lime juice of about 20° Tw., properly thickened, can be very well employed for resisting in laboratory experiments for iron and alumina mordants.

White Reserve (for Steam Alizarin).

Pink.

To

100 grs. gum water (100 per cent.)	1 gal.

add a solution of

12½ grs. sulphate of zinc	1¼lbs.

in

15 grs. water	1½lbs.

then add further

1 gr. caustic soda lye 50° Tw.	1¾oz.

diluted with

1 gr. water	2oz.

Tartrate of Chromium is also employed as resist for alizarin pink or rose, and is produced by reacting with tartaric acid on bichromate of potash as follows:—

50 grs. bichromate of soda or potash	5lbs.

are dissolved in

100 ccs. hot water	1 gal.

then add

60 grs. tartaric acid	6lbs.

when the reduction is complete, thicken with

50 to 60 grs. dextrine	5 to 6lbs.

Resist for Aniline Black.—No. 1.

100 grs. acetate of lime, 20° Tw	1 gal.
40 to 50 grs. dextrine	4 to 5lbs.

Resist No. 2.

In

100 cc. gum water	1 gal.

dissolve

5 grs. sulphocyanide of potassium or barium	½lb.

by adding other products with the sulphocyanide, coloured resists can be produced; for instance, by mixing lead salts with the resist, chrome yellow or orange can be afterwards developed.

By employing sulphocyanide of alumina or acetate of alumina with the other sulphocyanide, a red can also be developed where the black has been resisted.

No. 3.

40 grs. dextrine	4 lbs.

are dissolved in

100 grs. water	1 gal.
60 grs. arsenite of sodium, 70° Tw	6lbs.

No. 4.

Aluminate of soda thickened with dextrine or starch paste as

100 grs. aluminate of soda, 30° Tw (alkaline mordant)	1 gal.
30 to 40 grs. dextrin	3 to 4lbs.

White patterns under aniline black are now often produced by padding the goods with the aniline black colour, then printing on alkaline resist, and afterwards exposing the goods to ageing in the usual way.

DISCHARGES.

Some of the most important are the acid discharges on iron or alumina mordants, and give rise to the padding styles, which are, in fact, simply modifications of the alizarin dyed colours.

The goods are padded all over, or on one side only with the mordant, and dried, and afterwards the discharge is printed on, which, by dissolving the iron or alumina mordant where it is applied, prevents any colour from being formed there, and therefore causes the production of white spots on coloured ground, when the goods are dyed in alizarin, &c.

The discharging process by acid had more importance formerly than it has now, not only because the madder styles themselves are not so much in vogue, but also since block printing has yielded the place to machine printing.

Formerly it was a cheaper process to produce white spots on coloured ground by the padding method, since the same block could be used over and over again, but since the development of dried colour printing the patterns can be produced on the roller by engraving only the coloured ground, and leaving the white pattern unengraved, but it must be said that the discharging processes generally give clear and sharp lined whites which cannot be so well obtained by the direct processes, and this is the reason why the discharging methods, although more expensive and complicated, are still employed.

In the preparation of acid discharges, citric acid or lime juice is generally employed. The following recipes will give an illustration of an acid discharge.

Acid Discharge.—No. 1. (For Laboratory Work.)

100 grs. water	1 gal.
15 grs. starch	1½lbs.

boil, and while still hot, dissolve in

50 grs. citric acid crystals	5lbs.

For light mordants this colour can be diluted with more starch paste.

Acid Discharge.—No. 2.

100 grs. lime juice, 30° Tw	1 gal.
10 grs. starch	1lb.

boil, and when almost cold, add

10 grs. bisulphate of potash	1lb.

stir until dissolved.

Print on cloth which has been padded and dried twice with either iron or alumina mordant, dry, age, dung twice by the usual process, then dye with alizarin, &c.

White Discharge.—No. 3.

For goods to be dyed black with logwood, for mourning articles.

100 grs. lime juice, 40° Tw.	1 gal.
50 cc. water	½ gal.
20 cc. starch	2lbs.

boil, then cool to about 30° C. and add a mixture of

50 grs. sulphuric acid, 66° Bé	5lbs.

previously mixed with

15 cc. water	1½ gal.
10 grs. soda ash	1 gal.

This colour can be further reduced with starch paste.

Print on cloth which has been padded with a mixture of two parts acetate of iron, and one part acetate of alumina, at 6° Tw. and dried. After the discharge has been printed on, the goods are passed through the steam ager for one minute, left in bundle over night, then dunged, washed and dried with the dyewoods in about the following proportions to each other:—forty parts logwood, five quercitron bark, two sumach, along with twenty parts cowdung and two of glue solution.

TURKEY REDS.

Turkey red goods obtained by the discharging process after dyeing are produced in very large quantities, and form a very important branch of export to Eastern markets. The cloth is first of all dyed Turkey red, and then the patterns are produced by discharging, and thus whites, yellows, blues, greens and blacks are obtained on red ground.

Before going over to the discharging process it will be necessary to mention the dyeing of the Turkey red itself.

Turkey red dyeing has experienced a complete transformation in the last 10 or 15 years, and much progress has been made in this branch of industry, but in spite of this we are as much in the dark now about the theory of the formation of the brilliant red lake on the fibre as we were 20 years ago, in fact the theory has still to be made. It is especially in the important preparatory process of the oiling of the goods where no satisfactory explanation has yet been given.

We have seen a new method of oiling of the goods introduced into practice, and we have seen the old emulsive or Gallipoli oil (the *huile tournante* of the French) to a great extent driven out of the Turkey red dye works by the modern preparations from castor oil, and we may see perhaps the latter superseding the former completely; but even then we shall probably not have an explanation of the theory of its employment.

Turkey red dyeing, as many other useful arts, has come to us from the East, and judging by its name, it must have been through Turkey that it has penetrated into Europe; in fact the town of Adrianopolis was at one time famous for the reds it produced, and both in French and Italian the name for Turkey red is Adrianople red. The processes, as they were originally practised, varied of course greatly from those at present in vogue, and like all other industries, Turkey red dyeing has passed through several stages of progress. At the time of madder dyeing great improvements were made in shortening the length of the processes, and also in reducing to a minimum the amount of the raw materials employed. At one time as much as 50 per cent. of emulsive oil was used for the oiling of the goods, while the amount of alum was also over 50 per cent., and as far as madder was concerned 150 160 per cent. of the weight of the cotton was believed to be necessary for obtaining full shades. Little by little these amounts came to be considerably reduced and brought down to more reasonable proportions. The time employed was at first also very long, and was originally counted by weeks, then by days, until in some works it was boasted that a good Turkey red on yarn could be dyed in three days, and I know of an old dyer who could accomplish this feat, although the process in ordinary work would take much longer, but within the knowledge of the author it was actually done in some cases. The introduction of garancine at the time also brought about a further improvement, and the clearing processes were also considerably shortened.

But artificial alizarin has caused the great revolution in the practice of Turkey red dyeing, and the transformation has been completed by the introduction of the Turkey red or alizarin oils.

But we are not yet at the end of the transformation in this industry, and no doubt a quicker method of dyeing will be introduced at some future time.

We are now in a transitory stage between the old method of the Turkey red dyeing and the processes of the future, which will be introduced when we attain more knowledge as to the theory of its formation than we now possess.

The older processes required the cotton to be oiled several times (six or more), and each treatment with the oil was followed by long exposure in the fields; later on stoves were introduced, and the number of oil passages was little by little reduced, until ultimately three passages were found sufficient, while by the modern processes one previous passage in a good castor oil preparation is deemed sufficient to produce a good colour.

Alizarin was introduced into the Turkey red dye works in 1871 and 1872; and in 1873, in some of the principal Turkey red dye works in Switzerland the alizarin had displaced madder completely, and this in spite of the high price at which alizarin was sold at that time. The speedy success of artificial alizarin was due principally to the brighter shades that could be obtained, and the shortening of the processes, which did not then require such heavy preparation of the yarns, and such severe and expensive brightening operations, although it must be said also that the Turkey red yarn dyed with alizarin was received at the time with great mistrust, and encountered some opposition at the hands of the weavers, who complained that the cotton was too greasy and could not be easily sized for weaving. There was in fact a certain amount of truth in this complaint, since the yarns which were dyed at the beginning were dyed on cotton which had undergone the same oiling operations as for madder, but had not been exposed to the long boiling in soap and soda when brightening as by the old process, and therefore all the useless fat had not been removed, but this difficulty was soon got over, and alizarin established itself in the practice of the works, although it was maintained by many dyers that the new reds could not be so fast as those obtained by means of madder. This assertion was also easily disposed of when the new reds had been fairly tried, and the goods produced found to answer just as well as those obtained by the madder process, which could never have produced the bright shades obtained by alizarin. Although Turkey red goods are now mostly produced by means of the artificially prepared

Turkey red oils or alizarin oils, olive oil has not been completely abandoned, as some establishments still use the latter for the oiling of their goods, and employ, in a certain way, a modified form of the old and classic process of Turkey red dyeing, and some still employ two weeks, and some even four weeks, in the production of their reds, and claim to obtain better results than by the new and shorter process,—in fact some dyers go so far as to assert that truly fast colours can only be obtained by oiling the goods in the old fashioned way, and that the reds produced by means of modern Turkey red oils, although of very bright shade, do not come to the others in point of fastness.

The practical methods of dyeing reds with alizarin on cotton cloth can be divided into three classes:—

1st.—Those produced by the long process, with emulsive oils.

2nd.—Those produced by the short method with prepared alizarin oils, in which the cloth is oiled before dyeing.

3rd.—Those produced without any previous oil bath, but in which the oil is applied after dyeing.

The old process undoubtedly produces the fastest colours, which stand soaping and light, and especially bleaching, better than if produced by a short process.

The long process has been described over and over again in old and recent English publications, and therefore need not be described here, where only the series of operations will be indicated, just to show the difference when compared with the shorter methods.

In dyeing plain reds which have not to be discharged, the cloth is not bleached with chlorine, but is simply scoured and cleaned, as mentioned in the bleaching operations.

For goods which are to be discharged a previous bleaching is performed, care being taken that the cloth be not over-bleached, since experience has shown that the deepest reds are obtained on cloth which is not bleached at all, while brighter shades are produced if the cloth has been very carefully bleached, or, in fact, only half bleached, but thoroughly well cleansed, while over-bleached cotton gives the worst results. In order to insure the best shades, the cloth after scouring and cleaning should be bleached with sodium hypochlorite solution, instead of using the lime compound.

LONG PROCESS OF TURKEY RED DYEING.

The repeated passages in an emulsion of rancid olive oil and soda, or potash lye, are now employed for yarn dyeing, but scarcely ever used for cloth.

The modern long process is as follows:

1st.—Passage of the dry cloth through hot gallipoli oil, at about 110° C. on the padding machine, which removes at the same time the excess of oil.

2nd.—Exposure in stoves for 2 hours at 70° C.

3rd.—Passage through bath of carbonate of soda at 4° Tw. and exposed to stove for 2 hours at 75° C.; the two operations being repeated seven times.

4th.—Passage through carbonate of soda at ½° Tw., 40° C., washing with water and drying.

5th.—Passage through mordant of alum, dissolved in water, with the addition of 25 per cent. of its weight of soda crystals, showing 1° Tw. at 45° C. Steeping for 25 hours and washing, or using a stronger mordant and drying in stove, and then passing through weak soda lye, and washing as before.

6th.—Dyeing for 100lbs. cotton—

7 to 8lbs. alizarin, 20 per cent.
3lbs. sumach
30lbs. blood

and a small amount of chalk, if the water is not calcareous of itself; dyeing 1 hour up to the boil, and boiling 1 hour.

7th.—(1) Brightening in copper boiler for 4 hours at 4lbs. pressure, with 3 per cent. crystals, 3 per cent. soap to weight of cotton. (2) Brightening 2 hours at 4lbs. pressure with 2½ per cent soap, .15 per cent. tin crystals.

8th.—Washing and drying.

SHORT PROCESS OF TURKEY RED DYEING.

The cloth is, after scouring or bleaching, and drying,

1st.—Treated with a solution of alizarin oil at 5 to 10 per cent., according to strength of the product, on the padding machine, and dried on cylinder.

2nd.—Passed through acetate of alumina mordant at 6 to 8° Tw., and dried.

3rd.—Aged through steam ager or ordinary ageing machine.

4th.—Dunged with binarseniate and chalk, or chalk and cow-dung, through the ordinary dunging machine, in which the cloth is passed in full width at a temperature of about 60° C.

5th.—Dyed with 7 to 8 per cent. alizarin.
2 per cent. alizarin oil.
$\frac{1}{4}$ to $\frac{1}{2}$ per cent. tannic acid.
going from ordinary temperature to about 70° C. in 1 to 1$\frac{1}{2}$ hours, and leaving $\frac{1}{2}$ hour at this temperature.

6th.—Dried without washing.

7th.—Oiled with 5 per cent. solution of alizarin oil; dried.

8th.—Steamed 1 hour with or without pressure.

9th.—Soaped with 3 per cent. olive oil soap.

10th.—Washed and dried.

ALIZARIN RED.

The third method of dyeing red with alizarin, by employing the oil at the end only, yields shades, which, although very bright, cannot be compared in fastness to those produced by the longer processes, and although they are sometimes called Turkey reds, and are even discharged, they are best distinguished from the others as alizarin reds.

They are produced by two methods, one relying on the employment of acetate of alumina, the other on the employment of aluminate of soda.

Alizarin Red.—No 1. (with acetate of alumina).

1st.—Mordant the scoured or bleached dry cloth in acetate of alumina, 6 to 8 Tw., for which a basic acetate had better be employed. Dry, age in the ageing stove or machine, or in the steam ager, and leave in bundles over night.

2nd.—Dunging bath with arseniate or cow dung as usual; wash well.

3rd.—Dye in alizarin, alizarin oil and olein as before; wash and dry.

4th.—Oil bath with olein solution at 10 per cent.; dry.

5th.—Steam 1 hour.

6th.—Brighten with soap, &c., as before.

Alizarin Red.—No. 2. (with aluminate of soda).

The Schlieper's method of mordanting with aluminate of calcium has already been mentioned. The ordinary process is conducted as follows:—

1st.—Pad the dry cloth in aluminate of soda (alkaline mordant), at 10° Tw.; dry on cylinder.

2nd.—Fix the alumina on the fibre by a passage through sal ammoniac, or better, through an alum bath; wash and dry.

3rd.—Repeat No. 1 and No. 2. and wash well.

4th.—Dye as before.

The brightening process does not offer any special point of interest over the other methods.

The majority of plain reds on cloth are now dyed by the aluminate of soda process, which, by the employment of a very basic acetate of alumina in the mordanting operation, is rendered no longer or more expensive than the alkaline method, especially if one has a steam ager at command, through which the ageing can be started by a passage of one or two minutes, the cloth being allowed to lay in bundles for 24 hours, which completes the decomposition of the acetates. The other method, however, does away with ageing altogether, and is therefore preferred by those who have not at their disposal ageing machines or ageing rooms.

It is stated, however, by some practical men that the red produced by the alkaline mordant is not so fast as the one obtained by means of acetates, and this difference is especially apparent in the yellower shades, which contain anthra or flavopurpurin, the shades of which are by themselves not so fast as those produced by means of pure alizarin, which, as well known to practical dyers and printers, yields the bluest shades of red.

In Turkey red dyeing the yellower shades are sometimes preferred, and the alizarin works supply any shade that may be required, from the bluest to the yellowest; but some dyers or printers prefer to buy the pure alizarin, anthrapurpurin and flavopurpurin, and mix them according to their requirements.

In the production of Turkey red dyed or printed goods England stands in the front rank for the importance of the quantity produced, and as far as brightness of shade is concerned, the reds produced in Lancashire and Scotland are as fine as those which are produced by the best works on the Continent; but it must be said also that if the Continental production does not come up in quantity, the colours produced abroad are certainly not inferior to those produced in England. As far as the theory of Turkey red dyeing is concerned, there are, and have been for years, two theories; a chemical theory and a mechanical, or, rather, physical theory. *

While some maintain that the fatty substance takes part in the formation of the red lake, by forming chemical combination with alumina and alizarin, others maintain that the oil or fatty matter acts mechanically, by surrounding the alumina alizarin lake in such a way that it forms a kind of coating around the same, and makes it thus capable of standing the action of soaping and other reagents in a much better way than when not protected. The brightness of the Turkey red lake is also explained sometimes by comparison to a varnish, which imparts to a paint greater gloss and brilliancy; for instance, if an ordinary pigment colour is painted on wood, it has no gloss or brilliancy, but if a varnish is applied on the same colour then a quite different appearance will result.

In the author's opinion all these explanations are correct,

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* From a lecture by the author before the Society of Chemical Industry, in Manchester, January 29th, 1886.

if taken altogether; but they are open to objection if taken separately. The fatty substance combines really with alumina, and enters thus in the formation of the lake, acting also mechanically, by covering the lake so as to protect the same from the action of soap and other reagents, and as a kind of varnish, imparting greater brilliancy to the red.

A discussion has taken place sometime ago among Continental chemists on the theory of Turkey red dyeing, Müller-Jacobs, on one side, considers the prepared oils for Turkey red (which are obtained by treatment of olive or castor oil by means of sulphuric acid, washing with water, and neutralizing with an alkali) as a solution of the undecomposed oil in the alkaline sulpholeate or sulphoricinate, and this solution would act as a mordant, by giving up to the fibre the undecomposed oil in a very finely divided form, and therefore its action would rather be a physical than a chemical one, by enveloping the lake and thus protecting it from exterior influences.

Henry Schmid does not admit this physical theory, but maintains that the oil enters into the formation of the lake; he states that the oils will act as mordants, not only when prepared by means of sulphuric acid, but also if they have been treated in a different way. For instance, if castor oil is saponified by means of an acid, and the free fatty acid is separated and dissolved in alkali, the soap thus formed is very suitable for Turkey red dyeing.

He states further that an emulsion of oleic acid in water, obtained by very long shaking, can easily displace the sulpholeates in dyeing.

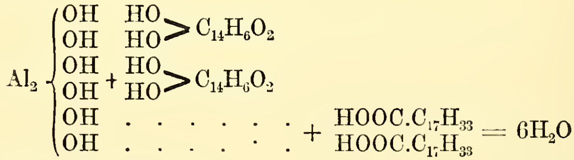
Liechti and Suida also propound a chemical theory, and have contributed very valuable researches on the formations of the sulpho compounds in the manufacture of prepared oils for Turkey red dyeing.

We will now consider what grounds we have for believing that the theory of Turkey red dyeing rests both on chemical and physical principles:

First of all, as the necessary ingredients for the formation of the Turkey red lake, we have alumina, then oil, then alizarin; these three are really the components of absolute necessity, and the principal constituents of the red; lime, of course, plays also an important part, and so does tin to a certain extent; tannic acid also plays a part, but only a secondary one.

Alumina, by whichever method it is fixed on the fibre, can be considered as hydrate of alumina more or less combined with the acid of the product originally employed; for instance, we might have a basic sulphate of alumina, which acts as mordant in the same way as pure hydrate of alumina. But let us suppose that we have pure hydrate of alumina on the fibre $Al_2(OH)_6$. We may also admit that we have pure alizarin at our disposal, and not insopurpurin or flavopurpurin, therefore $C_{14}H_6O_2(OH)_2$.

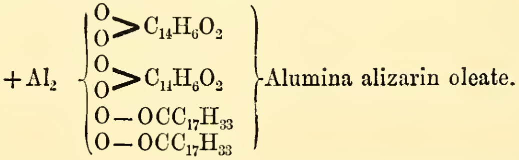
Then we have the oil, which by saponification would yield glycerine and the fatty acid; let us admit also in this case that we have free oleic acid at our disposal, $C_{17}A_{33}COOH$. We may remark here that, in the absence of proved facts, we simply make use of imagination to form a plan or theory, and possibly strike a formula, and bring forth reasons for the opinion in question. Let us suppose that the reaction could take place according to the following equations:—



$$Al_2\left\{\begin{array}{l}OH\\OH\\OH\\OH\\OH\\OH\end{array}\right. + \begin{array}{l}\left.\begin{array}{l}HO\\HO\end{array}\right> C_{14}H_6O_2\\ \left.\begin{array}{l}HO\\HO\end{array}\right> C_{14}H_6O_2\\ \ldots\ldots\ldots\\ \ldots\ldots\ldots\end{array} + \begin{array}{l}HOOC.C_{17}H_{33}\\HOOC.C_{17}H_{33}\end{array} = 6H_2O$$

Hydrate of alumina one molecule — Alizarin two molecules. — Oleic acid two molecules.

would form by elimination of water



$$+ Al_2\left\{\begin{array}{l}\left.\begin{array}{l}O\\O\end{array}\right> C_{14}H_6O_2\\ \left.\begin{array}{l}O\\O\end{array}\right> C_{14}H_6O_2\\ O-OCC_{17}H_{33}\\ O-OCC_{17}H_{33}\end{array}\right\}\text{Alumina alizarin oleate.}$$

Let us now examine if such a formula is possible. Experience has shown that good reds are obtained when, for 100lbs. of cotton, about the following proportions are used :—

Alumina mordant corresponding to
20lbs. of alum (potash alum)
Oil corresponding to
10lbs. fatty acid
7lbs. alizarin paste, 20 per cent., containing about
1·4lbs. dry alizarin.

Now the molecular weights are :—

$$\begin{array}{c}\text{For alum}\\ K_2Al_2(SO_4)+24H_2O\end{array} = 948{\cdot}14$$

$$\begin{array}{c}\text{Alizarine}\\ C_{14}H_8O_4\end{array} = 240 \qquad + \qquad \begin{array}{c}\text{Oleic acid}\\ C_{18}H_{34}O_2\end{array} = 282$$

As one molecule of alum corresponds to one molecule of hydrate of alumina, we would have :

Theory.	Practice.
948·14 alum, one molecule	20 alum
480 alizarin, two molecules	1·4 alizarin
564 oleic acid, two molecules	10 fatty acid

It will be seen that the amounts of fatty acid and alum correspond approximatively, but there is great difference between the alum and the alizarin. Although it must be said that neither the alum nor the oil will all be fixed on the fibre, and that of the mordants employed, perhaps only three-fourths of the amount of the alumina and of fatty acids are really fixed on the fibre, even then the quantity of alizarin which is found necessary, shows that the calculation of two molecules of alizarin for one of alum is too much. By taking one molecule of alizarin to one molecule of alum we should have :—

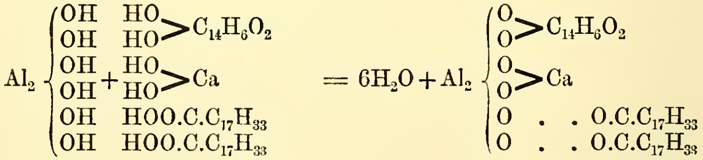
Theory.	Practice.
Alum 948	20 alum
Alizarin 240	1·4 alizarin
Oleic acid 564	10 fatty acid

Even in this case we have a great discrepancy between the amount of alumina necessary and that actually employed in comparison with the alizarin, and even admitting that a great excess of alum is used, in order to fix a small quantity of hydrate of alumina, still it is certain that in this case at least three times as much alum is used as is actually necessary.

But it is an old established fact that although cotton may have a certain amount of hydrate of alumina fixed on the fibre before soaping, the quantity greatly diminishes after the clearing or brightening process, and as was proved in madder dyeing the amount of alumina remaining on the fibre is always in a fixed proportion to the amount of the lime, also found on the fibre by incineration.

The quantity of alumina mordant employed to fix a certain amount of alizarin on the fibre, either by dyeing or printing, will be found to vary greatly in the different works, and comparing the processes and recipes published in the different books on calico printing, it will be found that there are not two authors who will give the same proportions of, say acetate of alumina and alizarin, but they mostly agree in giving an excess of alumina mordant.

Therefore, as it has been found in practice of dyeing that an excess of alumina is necessary, we may admit that one molecule of hydrate of alumina, and consequently of alum, would require one molecule of alizarin, then we should have still 2OH groups which would be taken up by lime, *i.e.*:



$$\mathrm{Al_2}\left\{\begin{array}{l}\left.\begin{array}{ll}\mathrm{OH} & \mathrm{HO}\\ \mathrm{OH} & \mathrm{HO}\end{array}\right>\mathrm{C_{14}H_6O_2}\\ \left.\begin{array}{ll}\mathrm{OH} & \mathrm{HO}\\ \mathrm{OH} & +\ \mathrm{HO}\end{array}\right>\mathrm{Ca}\\ \mathrm{OH}\quad \mathrm{HOO.C.C_{17}H_{33}}\\ \mathrm{OH}\quad \mathrm{HOO.C.C_{17}H_{33}}\end{array}\right. = 6\mathrm{H_2O} + \mathrm{Al_2}\left\{\begin{array}{l}\left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{C_{14}H_6O_2}\\ \left.\begin{array}{l}\mathrm{O}\\ \mathrm{O}\end{array}\right>\mathrm{Ca}\\ \mathrm{O}\ \ .\ \ .\ \mathrm{O.C.C_{17}H_{33}}\\ \mathrm{O}\ \ .\ \ .\ \mathrm{O.C.C_{17}H_{33}}\end{array}\right.$$

The ultimate formula would be lime, alizarin, oleic acid, alumina lake.

This formula, however, shows only one of the many possible formulas, since there are, in fact, no experimental proofs, or rather analytical proofs, that two or more molecules of alizarin should not combine with the alumina, instead of one: and it is also not unlikely that the lime itself might combine with the alizarin, by taking up one valence, and thus form a lime alumina alizarate; the possible formulas are rather numerous. In the working of the above operations we simply intend to imply that there are good grounds for a thorough chemical theory, not wishing, however, to state that the formula should be exactly as we have put it down. In the case of the fatty acid, we have admitted that we had pure oleic acid to work upon; in fact, if a prepared oil is used, made by saponification of the acid, it is very likely that the fatty acid enters into the formation of the lake as such, and this, I believe, is actually the case when dyeing on alizarin red; the oily preparation which is used at the end very likely enters into the formation of the lake by the action of the steam to form a kind of alizarin alumina soap lake; I think in this case the fatty acid has not time to become modified, and enters as such in combination with the alumina. But it is different in the process of Turkey red, when the oil is applied at first on the cotton; in this case it is impossible to conceive that the fatty substance does not undergo any modification when exposed on the fibre to the action of the stoving or exposure to air; in the old process of Turkey red oiling we know for certain that the oil is modified by exposure to air, light, and heat, and that a modified oil mordant is really fixed on the fibre, and does not go away by washing; and when oiling by means of prepared oils, a similar process must take place, and a mordant become fixed on the fibre which does not go off when the cotton is washed; but it is not likely that the same modification of the oil takes place in the new as in the old oiling process. It is very likely that in both cases it is a kind of oxidation of the fatty acid which takes place—similar to the drying process of the linseed oil, but this fact has yet to be proved.

Liechti, Suida and Müller Jacobs speak of the formation of oxyoleic acid and oxystearic acid, and their further investigation will no doubt throw fresh light on this point. It may also be taken as probable that the modified oil does not pass through any molecular change, but simply adds oxygen, no change taking place in the acid radicle, and that it is again capable of combining with alumina lime in the same way as before. Proof that the fatty acids enters really in chemical combination, seems to lie in the fact that both in the old and new process of Turkey red dyeing, a certain amount of heat and pressure is required for the formation of the bright reds, since by the old process the boiling in the dyebecks is necessary for developing the colour, and pressure is required to obtain bright shades; in the new process the steaming and also the brightening under pressure produces the same effect. In other words, it is by this heating that the real combination, in fact a saponification, takes place. We could chemically define an alizarin red as a colour in which oleic acid (or homologous fatty acids) forms with alumina, alizarin and lime in combination, a true soap lake.

In the true Turkey red we also form a soap lake, but the fatty acid is modified in such a way that it acts also physically by covering the lake and protecting the same from exterior influences.

The fact that in the old process of Turkey red such a large amount of the oil is used, speaks also in favour of the physical theory, and it is in my opinion due to the excess of modified oil that Turkey red colours owe their fastness against soapings, etc.

It will be remembered that in the old process of Turkey red, especially for dyeing with madder, sumach was generally used; the employment of this can be easily explained by admitting the formation of tannate of alumina, or rather the tannic acid of the sumach entering in combination with alumina forms a complex formula of alumina tannate, oleate, alizarate of lime.

There is evidently great analogy between the process which takes place when the goods are oiled for Turkey red dyeing, and that of drying linseed oil.

In both cases, if we were to employ the oils without any previous preparation, the processes would be much longer in taking effect, for instance, in the case of linseed oil, if we paint with the raw oil, it takes several days to dry, while the same oil after it has stood a proper treatment, such as is generally termed the boiling by means of a dryer, such as litharge, red lead, etc., it acquires the property to dry in much shorter time, in fact in a few hours.

If we take castor oil or olive oil in the natural state, they are not suitable for the process of Turkey red dyeing, or rather, would take too long to accomplish the same object which is done in a much shorter time when the oils undergo a proper preparation; in other words, we have to give to the olive oil or castor oil a treatment which, although different, bears great analogy to the process of the boiling of linseed oil.

From what has been said concerning the theory of Turkey red dyeing, it is evident that much remains to be done before the process can be properly explained, and there is plenty of scope for chemists to devote their time to scientific and practical researches in this interesting branch of industry.

Both the questions of oiling the goods and the drying of linseed oil ought to be studied at the same time, because there is some analogy between the two processes, although the ultimate results may be different, since olive and castor oil do not belong to the same class of oils as linseed oil.

It is also necessary that experiments should be conducted under the same conditions of exposure, temperature, etc., as they are conducted on the large scale; and the different reactions should not be tried by having the mordants in solution and reacting with alizarin, in order to precipitate the lakes, since the products thus obtained may not at all correspond to those obtained on the fibre.

Turkey red dyeing is a very promising field of chemical research, and it will certainly repay any chemist to devote his time, not only in trying to find out the theory of the process, but also to bring further improvements in this branch of industry.

DISCHARGES ON TURKEY RED.

White Discharge.—No. 1.

100 grs. tartaric acid solution, 60° Tw.	1 gal.
100 grs. acetic acid, 6° Tw.	1 gal.
100 grs. British gum	8 to 10lbs.

Print and dry, then pass in full width through a cistern or iron vat, supplied with rollers, over which the cloth travels up and down through a bath prepared with

100 grs. bleaching powder	1lb.
per 1 litre water	1 gal.

The cloth goes through at the rate of about 10 yards per minute, and in coming out of the bath is nipped between two rollers, which remove the excess of liquor, and is then passed through water and well washed.

To the discharging bath a certain amount of lime or chalk is added, in order to neutralise the free acid, which being brought by the pieces would accumulate to such an extent in the bath as to discharge the red altogether.

The reaction which takes place in this process is the combination of tartaric acid with the lime of the hypochlorite and the liberation of the hypochlorous acid, which reacts at once on the spot where the tartaric acid has been printed and destroys the red.

White Discharge.—No. 2.

100 grs. water	1 gal.
15 grs. starch	1½lbs.

boil, and while hot, dissolve in

60 grs. tartaric acid crystals	6lbs.

Owing to the high price of tartaric acid, substitutes have been sought in the process of discharging Turkey reds; the one which has been found successful, especially for white, is the arsenic acid which was originally recommended by Emile Kopp some years ago.

Yellow Discharge.—No. 1.

100 cc. lime juice, 40° Tw.	1 gal.
45 grs. tartaric acid crystals	4½lbs.
50 ,, acetate of lead	5lbs.
12½ grs. starch	1¼lbs.

boil, and when cold add

17½ grs. nitric acid, 60° Tw.	1¾lbs.

This colour is suitable for machine printing, while the following one is more suitable for the block, but could be made available also for the machine by removing the china clay, and adding a little more senegal gum.

Yellow Discharge.—No. 2.

100 cc. lime juice, 50° Tw.	1 gal.
50 cc. tartaric acid	4lbs.
40 cc. nitrate of lead	6lbs.

After dissolving thicken with

30 grs. china clay	3lbs.
30 grs. gum senegal	3lbs.

After printing and drying, the cloth is passed through the chlorine tank, then washed; the yellow is then raised in a weak bath of bichromate of potash, at 40° Tw., then through weak hydrochloric acid, and finally washed and dried.

Blue Discharge.—No. 1.

100 grs. water	1 gal.
15 grs. starch	1½lb.
5 grs. tragacanth gum	½lb.

boil, and while hot dissolve in

70 grs. tartaric acid	7lbs.
7½ grs. oxalic acid	¾lb.
30 grs. yellow prussiate of potash	3lbs.
30 grs. copperas	3lbs.

Greens are obtained by mixing the yellow and blue colours together, taking of the yellow discharge No. 1, and the following blue colour, either equal parts, or in proportion to shade required.

Blue Discharge.—No. 2.

20 grs. Prussian blue	2lbs.
20 grs. oxalic acid	2lbs.
50 cc. hot water	½ gal.

are ground together and allowed to stand over night, then mixed with the following thickening:

150 cc. water	1½ gal.
25 grs. starch	2½lbs.
40 grs. tartaric acid	4lbs.

Blue Black Discharge.

30 cc. logwood liquor, 8° Tw.	1½ gal.
70 cc. gall liquor, 8° Tw.	3½ gals.
20 grs. starch	10lbs.

boil, and while still hot add

2 grs. yellow prussiate	1¼lbs.

after cooling, add further

7½ grs. protochloride of iron, 60° Tw.	3¼lbs.
7½ grs. nitrate of iron, 80° Tw.	3½lbs.

Black.

100 grs. logwood liquor, 4° Tw.	1 gal.
20 grs. yellow prussiate	2 lbs.
25 grs. thick tragacanth water	2½lbs.
20 grs. starch	2lbs.

boil, then add

50 grs. iron liquor, 30° Tw.	5lbs.

and when quite cold, add further

12½ grs. nitrate of iron at 80° Tw.	1½lbs.

INDIGO PRINTS.

Patterns on indigo dyed goods are produced either by resisting or by discharging; the first method is not so largely used now as formerly, as by the discharging process clearer and neater impressions can be obtained.

The cotton cloth is first of all either fully bleached or simply scoured, according to the patterns which are required, the goods are then dyed, or as commonly termed, dipped, in the indigo vat.

The dyeing of cotton cloth in the indigo vat has not experienced much change in late years, except that the continuous dyeing machines have come more prominently into use in preference to the round vats formerly employed.

The machinery now mostly in use consists of a square tank generally imbedded into the ground, through which the cloth is passed in its full width over a system of rollers. The methods of reduction now mostly used in print works are those relying on the employment of zinc powder, commonly called composition, and the Schützember and Delalande process with hydrosulphites, which have been so fully described in all English publications of the last 12 years. As a rule the reduction on the indigo is effected in tubs, and then the necessary quantity is added to the dye vats.

After dyeing, the goods are soured to remove the lime and other impurities, and well washed and dried, and are then ready for the discharging.

White Discharge.

100 cc. water	1 gal,
100 grs. bichromate of soda or potash	10lbs.
85 grs. caustic soda lye, 60° Tw.	8½lbs.

Dissolve hot and thicken with

75 grs. calcined starch	8½lbs.

This colour can be diluted with starch or other thickening if necessary, as the discharge must be arranged according to the blue ground on the goods.

Yellow Discharge.—No. 1.

10 grs. gum water (1 : 1)	1lb.
15 grs. neutral chromate of potash or soda	1½lb
150 grs chrome yellow paste, 60 per cent.	15lbs.

Mix luke-warm, then when the bichromate has been completely dissolved, cool and add

75 grs. blood or egg albumen solution (as below) 7½lbs.

Albumen Solution.

100 grs. albumen	10lbs.
100 grs. water	1 gal.
2¼ grs. turpentine	4oz.
2½ grs. ammonia	4oz.

are mixed cold and stirred until dissolved.

Yellow Discharge.—No. 2.

10 cc. water	1lb.
7½ grs. bichromate of soda or potash	¾lb.
7½ grs. soda crystals	¾lb.

are dissolved and then mixed with

7½ grs. starch	¾lb.
10 cc. tragacanth water, 6 per cent.	1lb.
150 grs. chrome yellow paste, 60 per cent.	15lbs.

boil, stir until cold, and add

75 grs. blood albumen solution	7½lbs.

Red Discharge.

100 grs. water	1 gal.
20 grs. bichromate of potash	2lbs.
20 grs. soda	2lbs.

dissolve and then add

240 grs. vermilion finely pulverised	24lbs.
80 grs. starch	8lbs.
30 grs. tragacanth water, 6 per cent.	3lbs.

Stir into a paste, boil, and when cold add

140 grs. solution of blood albumen.	14lbs.

The above recipes may serve as examples for the preparation of coloured discharges by any of the pigments, such as orange, buffs, chrome greens, &c., which stand the acid treatment given in the bath which follows, for the discharging of the indigo and the fixing of the colours where the white has been printed.

The discharging and fixing bath consists of a warm solution of sulphuric and oxalic acid in water, the acids by the reaction of bichromate liberate the chromic acid, which at once destroys the indigo by converting the same into isatine on the spots where the discharge has been printed, and fixes at the same time any of the pigment colours by coagulating the albumen.

This fixing bath is prepared with sulphuric acid at 10 to 12° Tw., in which is dissolved

5 grs. oxalic acid	½lb.
to 100 cc. of liquor	1 gal.

the temperature being kept at 100 to 120° F., or about 45° C. The goods are passed through this bath on the padding machine, for a couple of minutes, then washed.

By this method white and coloured patterns, such as reds, yellows, oranges, greens, olives, browns, &c., can be produced by means of the respective pigments on a blue ground.

Many other methods of discharging the indigoes have been recommended, very few of them being of practical utility; among these discharging methods repeated trials have been made to produce a red discharge, containing the alumina mordant, which could afterwards be dyed in alizarin, and with a certain amount of success, but the red obtained is never a very bright one, as its beauty is marred by a small amount of the impurities contained in the indigo which have not been completely bleached, and also to some extent by the metallic oxide of the compound which is employed as discharging agent.

The following recipe may be taken as an example:

Indigo Discharge.

For alizarin red dyeing and other colours—

20 grs. peroxyde of manganese	2lbs.
75 grs. aluminium chloride	7½lbs.
50 grs. calcined starch	5lbs.
100 grs. water	1 gal.

Print on indigo dyed cloth, steam one hour without pressure, then wash first with warm water, then with cold, and dye (preferably after a short dunging), in alizarin or any other colours such as fustic, bark, or cerulein olive, &c. By this method there is, however, danger of rottening the cloth by the acid developed during the steaming.

Different methods of discharging have been used, such as the preparation of the cloth with bichromate of potash, and then printing on a hot acid discharge, consisting of oxalic and sulphuric acid, but the other method is preferable.

Red prussiate has also been used as a discharging agent in connection with caustic soda or potash, and also by the steaming method in connection with bicarbonate of soda, but the high price of the red prussiate prevents the process from being more extensively applied.

The chlorates of soda, in connection with vanadium and the chromium and aluminium chlorates, have also been tried, but these processes have not gone out of the stage of experiment. Since the introduction of Schlieper's glucose process the methods of discharging of dipped indigoes with fixation of alumina mordant at the same time, have lost their importance since the effects of red and blues, with white ground or without, can be more cheaply and effectively produced by the newer method. It is easily conceived also, that instead of dipping indigoes, the pieces can be printed or rather padded on one or both sides by the glucose process, and then discharged by the bichromate of potash method.

If the price of red prussiate of potash was not a hindrance, the method of discharging with this agent would undoubtedly find a more extensive application, since pigment colours and albumen can be mixed with the discharge, and thus colours fixed at the same time that the discharging is being effected; and the pigments by the steaming are even more permanently fixed than by means of the hot acid bath in the bichromate method, and a greater variety of colours can also be produced by employing other pigments which are affected by the passage in acid.

As a steam discharge red prussiate can be simply mixed with caustic soda and properly thickened, while if, instead of caustic soda the aluminate of soda is employed, then alumina is fixed on the fibre; at the same time, as the steaming injuriously effects the indigo blue, the process can be modified as follows:

Red Prussiate Discharge.

100 grs. water	1 gal.
100 grs. acetate of alumina, 20° Tw.	1 gal.
200 grs. red prussiate of potash	20lbs.
20 grs. acetic acid, 9° Tw.	2lbs.
200 grs. calcined starch	20lbs.

Print on indigo blue cloth, dry, and pass through soda lye at 20° Tw., at a temperature of 45° C.; wash well and dye in alizarin, &c.

The discharging by electricity has been recommended by Goppelsroeder, and if the method is as yet not a practical one, it is certainly very interesting.

White or coloured patterns are also effected on indigo dyed goods by the resisting process, but this is not so much used now as formerly, and the following recipes may serve for illustration.

White Resist.—No. 1.

100 grs. water	1 gal.
25 grs. sulphate of copper	2½lbs.
25 grs. sulphate of zinc	2½lbs.

heat gently until dissolved; thicken with

20 grs. flour	2lbs.
5 grs. British gum	½lb.

White Resist.—No. 2.

100 cc. water	1 gal.
20 grs. starch	2lbs.
10 grs. British gum	1lb.

boil, and while still lukewarm dissolve in

50 grs. copper sulphate	5lbs.
25 grs. zinc sulphate	2½lbs.
12½ grs. nitrate of copper solution, 70° Tw.	1¼lbs.

Yellow Resist.

100 cc. water	1 gal.
100 grs. copper sulphate	10lbs.
100 grs. nitrate of lead	10lbs.

dissolve, then add

60 grs. flour	6lbs
100 grs. sulphate of lead paste	10lbs.

(the bye-product of acetate of alumina preparation).

boil well and stir until cold; print and dry; dye cloth in the vat, then pass through weak sulphuric acid, wash, and pass through bichromate solution containing

12 grs. bichromate of potash	2oz.
in 1 litre water	1 gal.

(at a temperature of 100° F.)

wash, then pass through hydrochloric acid bath, at ½° Tw., containing

6 grs. oxalic acid	1oz.
per 1 litre liquor	1 gal.

Orange Resist.

This colour is prepared in the same way as for the yellow, but instead of the water the following lead preparation is taken:

Orange Standard.

1 litre water	1 gal.
400 grs. acetate of lead	4lbs.
200 grs. litharge	2lbs.

boil until all the litharge becomes white, replace the water which has evaporated, leave to settle, and use the clear liquor.

Print, dry, then dye the cloth in the vat, and give the same treatment as for yellow, but after the oxalic and hydrochloric acid bath, pass the goods through a bath at 180° F., prepared in the proportion of

1 litre water	30 gals.
3 grs. bichromate	1lb.

and enough slacked lime to give a milky appearance to the bath; work in this bath until the orange attains the required shade, then wash well and dry.

In the production of the Lazulite style, mordants for red, purples, chocolates, &c., are introduced in the resist, and the cloth, after dyeing in indigo, is dyed with alizarin, but these styles are now seldom employed.

The following colour for fixing alumina mordant while resisting the blue, may be found interesting.

Resist Red.

200 grs. nitrate of zinc, 36° Tw	1 gal.
50 cc. water, tinted with magenta or peachwood.	½ gal.
25 grs. alum	2½lbs.
20 grs. acetate of lead	2lbs.

heat until the alum is completely dissolved, stir until cold and boil with

15 grs. starch	1½lbs.
5 grs. British gum	½lb.

For lighter shades reduce with more thickening.

In the preparation of the indigo vats the zinc, hydrosulphite and copperas methods are employed. Some printers prefer the one, some the other; if well managed they all give good results.

It is not intended here to go into the details of the preparation of the different vats, which have been fully described in English text books relating to dyeing or printing, but the proportions will be given, which are only intended to convey an idea how the vats are prepared, since the proportions vary considerably in the different works.

Copperas Vat.

5 grs. indigo	1lb.
10 grs. copperas	2lbs.
15 grs. lime	3lbs.

Zinc Vat.

5 grs. indigo	1lb.
10 grs. zinc	2lbs.
10 grs. lime	2lbs.

For both vats the amount of water varies according to the shade required, but the following may be taken as an example:

500 cc. for dark shades	10 gals.
1000 cc. for lighter colours	20 gals.

Hydrosulphite Vat.

10 grs. indigo	1lb.
10 to 15 grs. milk of lime	1 to 1½lb.

200 grs. CaO per litre.
2lbs. CaO per gallon

and as much hydrosulphite, at 40° Tw., as produced from

80 to 100 grs. bisulphite of soda ....8 to 10lbs.

The whole is mixed, and when the reduction is complete the product is kept in stock and added to the vat in proportion to depth of shade required.

Preparation of Hydrosulphite.

This is also called hyposulphite by some chemists, and is produced as follows: Take for

1 litre bisulphite of soda, 55° Tw. .... 1 gal.

about

100 to 120 grs. zinc foils, or granulated or zinc powder...1 to 1½lb.

place in a vessel supplied with an agitator, and allow to react for about one hour, then let the liquor run off from the zinc, which can be employed for the next operation, and use the hydrosulphite at once.

In this preparation half of the zinc originally employed is dissolved to form the hydrosulphite, consequently in the next operation the zinc dissolved out is replaced by fresh metal. The liquor obtained shows about 60° Tw.

MANGANESE BRONZE COLOURS.

This style has not been largely produced in the last few years. The pieces are padded in a solution of sulphate or chloride of manganese, at about 80° Tw., dried, and passed twice through soda lye, first at 24° Tw., and the second time at half that strength, the hydrate of the manganese is thus precipitated on the fibre. After washing, the pieces are passed through a solution of bleaching powder, showing 2° Tw., in order to form a hydrated peroxide; they are then washed and dried. The process of discharging relies on the employment of proto-chloride of tin (stannous chloride), which reduces the peroxide of manganese to the protoxide, while the tin salt is converted into stannic acid, and the hydrochloric acid thus liberated dissolves out the manganese by forming the chloride of manganese, which is then removed by the washing which follows. Other products can be connected with the stannous chloride, and thus coloured discharges can be produced on brown or bronze ground.

White Discharge.

100 cc. hot water	1 gal.
40 grs. light British gum	4lbs.

boil and when dissolved add

50 grs. stannous chloride solution, 12° Tw	5lbs.
40 grs. tartaric acid	4lbs.

Blue Discharge.

100 cc. water	1 gal.
15 grs. starch	1½lb.
10 grs. light British gum	1lb.
7 grs. yellow prussiate	¾lb.

boil, then add while still hot

20 grs. tartaric acid	2lbs.
10 grs. oxalic acid	1lb.
5 grs. nitrate of iron	½lb.

before use add five parts by measure of this standard to three parts stannous chloride solution, 120° Tw.

Yellow Discharge.

100 cc. hot water	1 gal.
40 grs. dextrine	4lbs.
50 grs. nitrate of lead	5lbs.

heat until dissolved, then add

40 grs. tartaric acid	4lbs.

Before printing mix three parts of this colour with one part of stannous chloride, 120° Tw.

The yellow must be afterwards raised by passing through bichrome in the usual way.

Green is obtained by mixing the yellow and blue colour.

The black is either an iron logwood black, or an aniline black, simply printed on without any tin.

Red Discharge.

100 cc. peachwood solution, 15° Tw.	1 gal.
20 grs. starch	2lbs.
1½ grs. copper sulphate	2½oz.
1½ grs. sal ammoniac	2½oz.

boil, then add

5 grs. stannous chloride solution, 120° Tw.	8oz.

and before printing, mix two parts of this colour with one part stannous chloride, 120° Tw.

All these discharges are printed on the bronze-dyed cloth, and after printing, the pieces are hung up; they are then well washed, passed through a chalk bath, and washed again, if they then contain blue or green, they are passed through the bichrome bath, then washed and finally dried.

The manganese bronze style, and the so-called spirit styles are very little used at present.

BENZOPURPURIN AND ALLIED DYESTUFFS.

Benzopurpurin 4B (blueish shade of benzopurpurin), on Cotton.

Dye, boiling one hour with

5 per cent. carbonate of potash.
2½ per cent. soap.
3 per cent. benzopurpurin 4B.

Instead of carbonate of potash the following alkaline mordants will also do.

5—10 per cent. phosphate of soda.
5 per cent. soda crystals.
5 per cent. borax.
5 per cent silicate of soda.
5 per cent. stannate of soda.
5 per cent. glauber salt.

In order to get a colour resisting light and air still better, the goods can be taken, after dyeing, through a second cold bath, to which is added

5 per cent. soda crystals.

A brighter and deeper shade of red is got by giving the goods, after dyeing, a second cold bath, to which is added

5—10 per cent. Turkey red oil solution.

This Turkey red oil solution is made up as follows:

5 parts soda.

dissolved in

75 parts water.

then

25 parts Turkey red oil (neutral)

added, and the whole well mixed. After taking the goods through the above mentioned cold water (with 10 per cent. of this Turkey red oil solution added), dry, without further washing. If this Turkey red oil bath is applied, of course, the soda bath mentioned above is left out. The benzopurpurin 4B goes much fuller and deeper in shade on the fibre than the 1B, and the shade is considerably bluer. The dyebaths are kept for further use, and for new lots of cotton, proportionately less colour and mordant have to be added to the bath.

Benzopurpurin B.

Use

2 to 2½ per cent. carbonate of potash.

Short liquors are to be recommended.

Benzo-Azurine.

Dye, boiling for one hour with

5—10 per cent. glauber salt.
2½ per cent soap.

and

2—3½ benzoazurine.

according to the shade required. (Instead of the glauber salt, 5 to 20 per cent. phosphate of soda may be added.) The goods are well washed after dyeing, and, in order to clean them from any dyestuffs which may have remained mechanically adhering to the fibre, it is even advisable to wash them through a lukewarm soap-bath first, and afterwards again through a cold water bath, which latter has shown to develop the colour still brighter than is turned out in the dyebath. If indigo shades are wanted, the addition to the dyebath of a small quantity of chrysamine—which must be thoroughly dissolved in boiling water before adding to the bath—gives splendid results. To 100 parts of benzo-azurine, 1—2½ parts of chrysamine powder—according to the shade of indigo required—are added. All such shades dyed with benzo-azurine, and chrysamine, have the great advantage against indigo that the cotton goods do not rub off nor wash out. Besides the benzo-azurine blue is also fast against light, air, and acids. The dyebaths are kept for further use; and for new lots of cotton, proportionately less colour and mordant is added to the dyebath. Benzo-azurine (just as well as the chrysamine, our benzopurpurin, and azo-blue, has the peculiar property of acting as a mordant by itself, so that, if the cotton is first dyed with a bottom of benzo-azurine—any other aniline colour (magenta, saffranine, eosine, Bordeaux, methyl violet, benzaldehyde green, etc)—may be dyed on the cotton without needing to add any other mordant for topping, thereby facilitating any shading off into other tints immensely.

Azo-Blue.

Dye either with

7 per cent. phosphate of soda, Na_2HPO.

and common or black soap, or with

2—2½ per cent. carbonate of potash, K_2CO_3,

and

3½ per cent. colour.

Dye, boiling for one hour, when a reddish tinge will appear; lift, wash thoroughly in cold water, and dry in an airy room, when the blue shade will reappear (if dried at a high temperature the colour will again become reddish, but lose this tinge again when the cotton has cooled). The first bath not being exhausted, one may continue to dye on it, thus using for further parcels less, or only half the former quantity of colour or mordant; of the latter there is no more to be added. This colour is very fast to washing, as well as to light, air and acid.

Chrysamine on Cotton.

For a medium yellow shade, dye with

7 per cent. phosphate of soda, Na_2HPO, and olive oil, common or black soap.

or

3 per cent. silicate of soda and olive oil, common or black soap.

and

1 per cent. chrysamine in powder.

Raise the bath to boiling point, enter the yarn and dye for one hour, turning off steam. Should the dyeing be done at the boil a reddish yellow will appear. Wash well after dyeing. The first bath not being exhausted, one may continue to dye on it, thus using for further parcels less, or only half, the former quantity of colour or mordant; of the latter there is finally no more to be added. This colour dyes very even and resists soap.

The above colours are often dyed as a ground for aniline black patterns. The benzoazurine and benzopurpurin can also be discharged by the following processes.

White Discharge.

1½ litre water
160 grs. wheat starch
160 grs. dark calcined starch
boil, stir until cold, then add
100 grs. tin salt
100 grs. acetate of lime, 10° Bé.
Print; dry and steam half an hour.

Yellow Discharge.

920 grs. gum water
480 grs. berry extract, 30° Bé
320 grs. acetate of tin
240 grs. acetate of chrome 20° Bé
40 grs. tin salt.

There is only one drawback in the discharging of the benzoazurine blues; although fast to soap, they are apt to bleed or soil the white, when passed in a hot soap bath.

It is a great pity the reds produced with benzopurpurin are not faster to air and light.

The above recipes and information are due to the kindness of Messrs. Bryce and Rumpff, the agents of the Elberfield Colour Works.

MACHINERY AND APPARATUS

EMPLOYED IN CALICO PRINTING.

In this chapter will be described the machinery and apparatus employed in printing processes, on the large scale, and the different manipulations will also be mentioned.

The operations of the printworks may be divided in five general classes:—

1st.—Bleaching operations.

2nd.—Preparation of the printing colours.

3rd.—Application of the colours by printing on the cloth.

4th.—The fixing of the colours by direct processes or by dyeing.

5th.—Washing and cleansing of the printed goods, comprising also the soaping and bleaching with chlorine.

6th.—Finishing operations.

BLEACHING MACHINERY.

The bleaching has been fully discussed in that part of this work relating to it, and there is not much to add with regard to the machinery employed, which is illustrated by the plates.

It may here be observed that all calico printers do not do their own bleaching, and that in many cases the cloth is delivered ready bleached in the hands of the printers, especially in the export trade, when the cloth is bleached in this country, exported, and then printed at the place of consumption.

The following remarks may be found useful in regard to this industry:—In the singeing process the plate singeing by free fire is still pretty extensively used, and the revolving cylinders are also employed. The gas singeing machines seem however to be the most favoured ones, although the opinions of some old practical men lean to the older system.

A combination of the two principles of a revolving cylinder and the employment of gas has recently been effected; a copper cylinder being heated from the inside by a mixture of air and gas, and from the outside by a range of burners which form a flame line through which the cloth is forced to pass, while it touches the red hot cylinder at the same time.

The principle of electrical singeing has been mentioned before and need not be repeated here.

PREPARATION OF PRINTING COLOURS.

In all well fitted printworks the preparation of printing colours* is performed in a special department of the works, called the *colour shop*, and in many cases in a separate building altogether. This is advantageously placed either in communication with, or at short distance from the laboratory, in order to be under the control of the chemist or manager. The proper conduct of a colour shop requires extensive practical experience, and is generally entrusted to men of tried ability, since success in printing depends on a good preparation of the colours, along with a good application of them.

The Colour Pans.—The apparatus now mostly employed in all large works consist of a set of colour pans of different capacity, from one up to ten gallons, or even more, arranged in a row, as shown by the illustration (Plate VI). The pans are constructed of copper, being double cased, or, as it is called sometimes, jacketed, and by this means they can be heated by steam, which is introduced in the double

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* It must here be observed that all preparations for printing on fabrics are generally termed *colours*, although in the right sense they are not really such; for instance, thickened mordants, ready for printing, are termed colours, and even discharges are so termed; however, as this is the name generally employed in practice it has been kept here also.

case. The contents of the pans can also be cooled by allowing cold water to flow through the double case instead of the steam. Each pan is supplied therefore with steam and water taps, and is furnished with a water tap for filling the pans with water when preparing the colours, or for washing the pans. By a very practical and useful arrangement the pans can be tilted up or upset, and thus emptied.

The stirring of the colours was performed by hand, but now, in the majority of cases, by means of mechanical agitators, as shown in the illustration. These sets of pans are of different construction, according to the different makers, and in some cases they are so constructed that the pans are permanently fixed, and cannot be moved to remove the colours, and the pans have therefore to be emptied from the top, the colours being removed by means of a scoop or any other suitable vessel.

In preparing thickening or other colours in which starch enters, care must be taken to stir the starch first whilst cold, with water or the other ingredients, until it is rendered in fine state of division, and then to heat. Precaution is of course more necessary in working on the smaller scale, and heating on free fire, since every one will have made the observation, that if starch is boiled at once with hot water without previous stirring with cold water, to reduce it into a kind of pulp, that the thickening produced is not only lumpy but in some instances small blocks of starch have not been boiled, the water being prevented from penetrating through, by the paste formed at the exterior.

This precaution is not necessary with gums, which, on account of their solubility do not require any previous stirring or mixing with cold water, but can be mixed at once with hot water; in fact, in some cases not even colour pans are employed for dissolving the gums, but simply casks heated by direct steam.

Several colour pans are generally arranged to form a set on an iron frame, and arranged so that when heating by steam the outlet steam pipes are connected with a water trap, with the double object of preventing waste of steam, and collecting at the same time the hot water, which is always useful in a colour shop. The employment of these steam traps is found of great utility in all cases when using steam for heating double cased or jacketed pans or evaporators, as is the case in the manufacture of aniline and other colours. The preparation of the printing colours or thickenings do not offer any difficulty on the large scale, but it requires experienced men to successfully carry them out.

Straining.—When the colours are well prepared or mixed, they must undergo a very important operation, which is the straining; this has not only for its object the removal of any lumps or grit which may be found in them, but it effects a more thorough mixing and gives more homogeneity and softness to the mass. Many attempts have been made to devise apparatus for straining by mechanical means large quantities of colours at the same time, and several arrangements have been introduced, one or two of which have been found useful in printworks; but although successfully employed by some printers, they cannot be said to have been generally accepted in practice; in fact, the hand is still employed in the majority of cases for straining colours; and hand-straining would always be preferred if it were not expensive, not only on account of the labour, but also on account of the cost of straining cloths, which are very quickly used up.

The apparatus devised works on two different principles, either on the idea of pressing the colour through a metallic sieve or straining cloth, by means of heavy pressure, applied by aid of a cylinder; or by the inverse principle of forcing the colour to go through by means of the vacuum.

On the Continent, very often, metallic sieves are employed, through which the colour is allowed to pass by working, by means of a brush; this method works satisfactorily with many colours, only it has the drawback that very often the hairs of the brushes go through the sieve and along with the colours on the printing rollers, and thus cause irregularities.

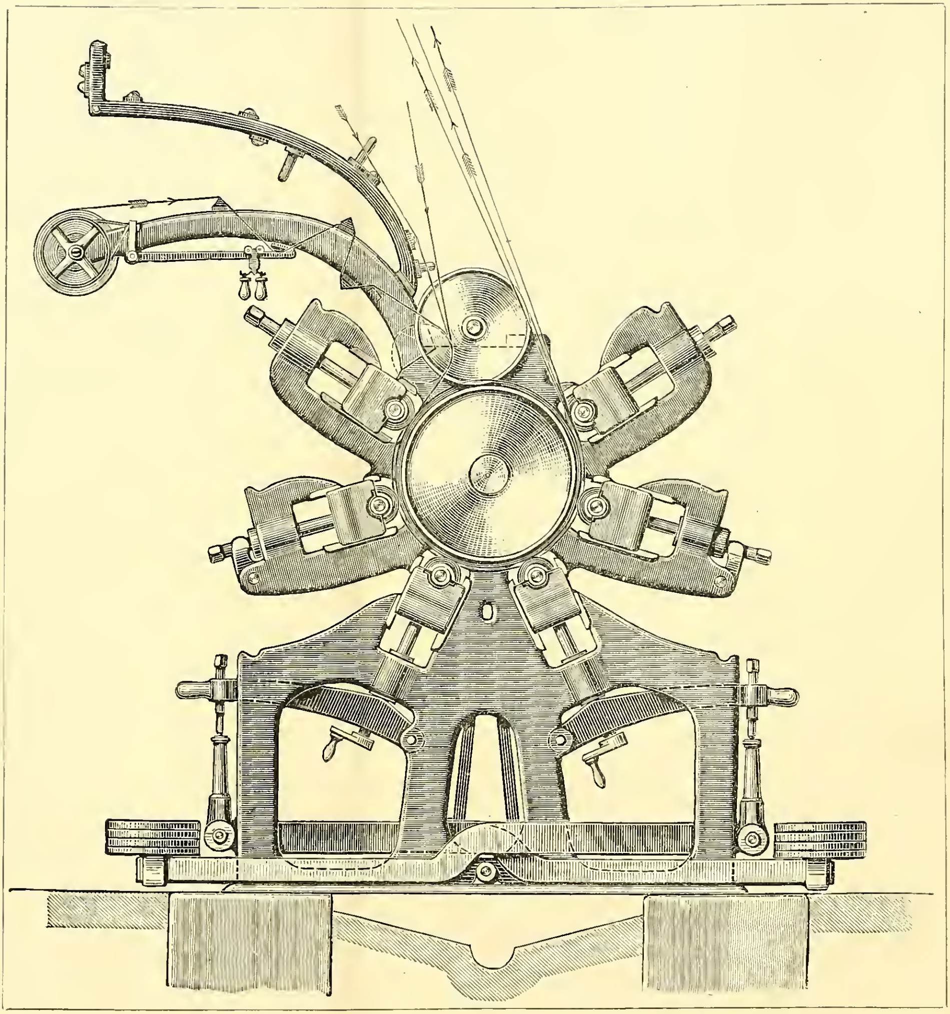

PLATE X.–6-COLOUR PRINTING MACHINE.

THE PRINTING MACHINE.

The printing machine consists of a large iron *bowl* or *drum,* revolving on its axis. The drum is covered with several layers of a coarse cloth called lapping, in order to form a kind of elastic cushion. This cloth is generally made of woollen weft and linen warp, and although coarse in texture must consist of good strong material, as it has to stand much strain. Lapping with india-rubber or gutta-percha prepared fabrics have not come in general use.

Against this bowl is pressed the engraved *copper cylinder.* which receives the colour from a *wooden cylinder,* covered with cloth, and revolving or dipping in the *colour-trough.*

In order to remove the surplus colour from the copper roller, the so-called *doctor* is supplied; this is simply a sharp blade, which is pressed at an angle on the roller, and scrapes off all the colour from the roller except that which is contained in the engraving.

In order to remove any loose threads or filaments, the so-called *lint-doctor* is also supplied, working on the other side of the roller, opposite to the *colour doctor.*

The cloth to be printed passes between the engraved copper roller and the bowl, and in order to have an elastic underlayer, it is supplied with the *blanket,* which is a thick, strong cloth, generally made of pure wool, and which is arranged as an endless web, both ends being carefully sewn together. For keeping the blanket clean, the *back cloth* is allowed to go between the blanket and the printing cloth. The back cloth is simply formed of grey cloth, which has afterwards to be bleached and printed in its turn.

The three cloths—that is, the blanket, the back cloth, and the printing cloth—go through at the same time between the bowl and the printing roller; the latter gives the colour kept in the engraving over to the printing cloth next to it, and this giving up is caused, first, by the pressure of the printing roller against the drum, and secondly, by the action of the lapping and the blanket, which, by forming a kind of elastic cushion, press the calico into the engraved cavities of the roller, and force the cloth to absorb the colour, which is prevented to spread over by the pressure asserted at the same time. India-rubber blankets are also used, but not so extensively as the ordinary woollen ones. For each colour one roller is necessary, and therefore a pattern containing more than one colour or shade requires a separate roller for each; each roller, of course, containing the engraving of the colour it has to give up to the cloth, and must be supplied with the other accessories of doctor, colour trough, cylinder, &c.

THE COPPER ROLLER.—This is a hollow cylinder, varying from ½ inch to 1½ inch in thickness, and is mounted on the iron *mandrill* or axis to revolve and be pressed against the iron drum.

Since for each colour a separate copper roller is required it will be easily understood that the stock of rollers in a large calico printing establishment must represent a very large monetary value, and repeated trials have been made to produce rollers by the electrical process. This has been accomplished with perfect success by depositing a thin layer of copper on a shell roller made of cast iron; these rollers work satisfactorily in some Manchester printworks; they are very cheap, and can easily be recoppered at a small expense, and if they have not come more into use it is on account of the cheapness of copper during the last few years, and of the fact that copper represents always an available capital, while such is not the case with the shell roller.

THE ENGRAVING of the copper rollers is done sometimes by hand, but more often by mechanical or chemical process. The hand method is of course more expensive, and only resorted to in special cases.

The mechanical method, or mill engraving, relies on the following principle:—The pattern to be engraved is cut by hand on a small cylinder of soft steel, which is then subjected to the process of hardening, and the design is then produced on another soft steel cylinder by heavy rolling pressure on specially constructed machinery. The second cylinder is then utilised to produce the design on the

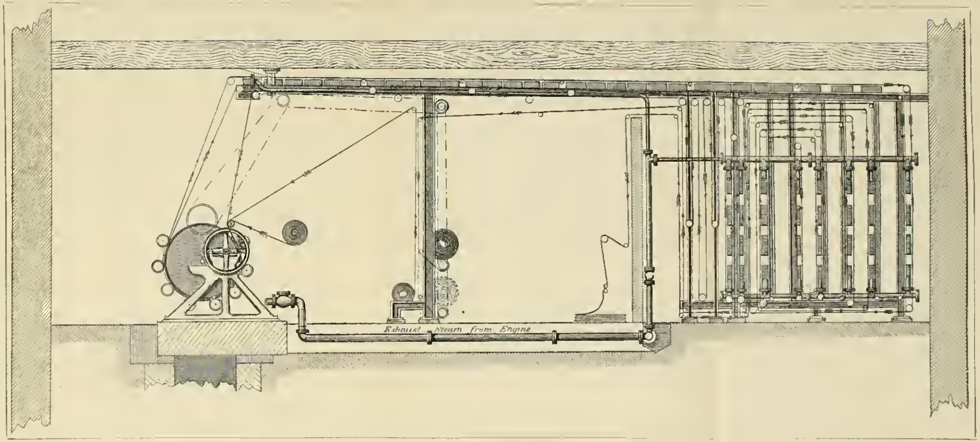

PLATE XI.—8-COLOUR PRINTING MACHINE, WITH DRYING ARRANGEMENT.

copper roller, on which it is pressed by heavy pressure on suitable machines, when the copper, being softer, easily takes the impression, the design being repeated all over the roller wherever required.

In the chemical process, or etching method, the copper roller is covered all over with a layer of varnish on which the design is cut through by a sharp point moved by means of the pentagraph machine, according to the design required; the varnish is removed by the sharp point and the copper is laid bare.

The roller is then immersed or rather allowed to revolve for a short time in a bath of weak nitric acid, sometimes along with chromic acid, when the copper is to a certain extent dissolved in the portions not protected by the varnish, and etched to a sufficient depth to carry the necessary amount of colour. It is finally washed and dried, and after the varnish has been removed the roller is, if necessary, polished, and is ready for the printing.

The Doctor or knife blade is from two to three inches broad and about $\frac{1}{20}$ of an inch in thickness, is generally made of steel, in special cases of brass or so-called composition, and often nickel plated. Great skill is required in the arrangement and especially in the sharpening of the doctor blade, as a good impression mostly depends upon it. By means of weights the pressure of the doctor is regulated on the revolving copper rollers.

The arrangements of printing machines are shown by the illustrations in Plates X., XI., and XII.*

A 12-colour machine may be considered of the largest type, since there are few patterns that contain more than 12 colours or shades; but one 20-colour machine exists, which was constructed by Thomas Gadd, of Salford.

The operations of printing on a large scale requires practical skill and experience, and must be learned by practice, as no amount of description would be of much assistance.

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* For these illustrations we are indebted to the kindness of Messrs. Mather & Platt.

The Drying of the cloth after printing is of great importance; in few cases only the cylinder can be used, but in the majority of cases the drying is effected by allowing the cloth to pass very closely, without touching, over a series of hollow cast iron plates or chests heated by steam. These chests are arranged in different ways, and other drying arrangements are also devised, in which hot air is employed; plates XI. and XII. will give an idea how the drying is effected, the drying of the blanket and back cloth being performed at the same time.

In the chapter relating to Indigo printing by the Glucose process will also be found illustrated the principle of hot air drying.

The drying of calico after preparing with oleine, or washing, soaping, &c., is generally performed on a series of cylinders heated by steam, because in this case there is no fear of spoiling the printed colours or mordants, or rottening the cloth by too high a temperature.

The Fixation of the colours, either by steaming or by dyeing methods, has already been fully described. Here will only be mentioned the machinery or apparatus employed. For *steaming*, two principles are now generally followed, relying in the employment,

1st. Of a closed iron steamer worked under pressure.

2nd. Of a continuous steamer constructed of brickwork or masonry.

The first apparatus is generally called a Steaming Cottage. It consists of a vertical shell boiler, closed at one end and supplied at the other end with a strong iron door which can be lifted up and down, so as to admit a carriage or truck on the iron rails laid at the bottom of the steamer.

The printed cloth is hung up on poles at the higher part of the carriage, being generally covered up or folded in grey pieces or woollen flannel.

The pressure employed varies according to the style of work, and the duration generally about one hour, seldom much more; the pressure commonly used is 4lbs. per square inch, seldom higher than 10lbs.

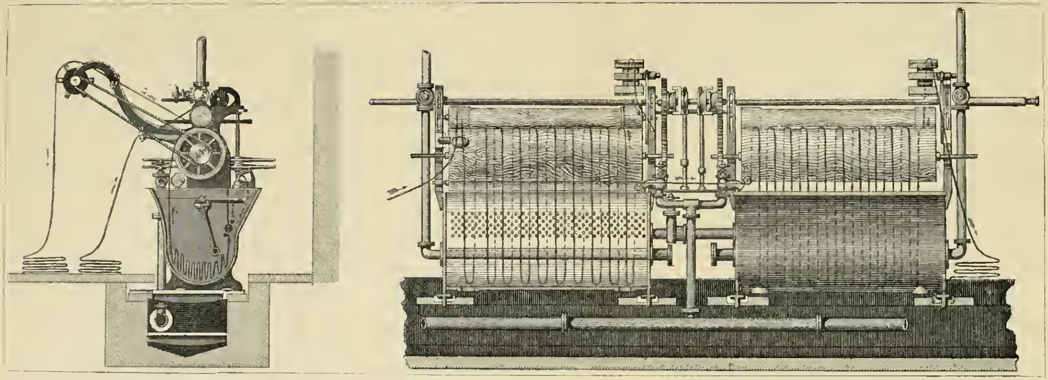


PLATE XIV.—SOAP BECKS.

THE CONTINUOUS STEAMER.—This is coming more and more into favour, owing to the large amount of work that can be turned out by one apparatus. More than one system is in use, but our illustration (Plate XIII.), shows the one constructed by Mather and Platt, in which will be seen the cloth entering on one side and coming out from the other.

The printed cloth, which is contained between two grey pieces, is hung up on poles, which are carried slowly on by means of a special chain arrangement from one side of the steamer to the other, when the cloth is removed by a suitable mechanical arrangement, and the pole sent back to the front and utilised for new pieces. The whole working of the apparatus is apparent by a glance at the illustration.

For colours which are fixed by other means, such as by ageing and dyeing, the apparatus has already been mentioned, and illustrations of steam-agers and dunging cisterns, &c., have already been given and need not be repeated here.

THE DYEING MACHINES FOR ALIZARIN DYEING.—Sometimes copper cased dyebecks (Plate IX) are employed for alizarin dyeing, but generally the heating is effected by means of steam, care being taken that it spreads evenly, or else uneven dyeing will result. This dyeing machine is composed of an oblong cast iron beck, at the top of which is fixed an angular revolving wooden wince, over which the cloth is allowed to pass in spirals and fall in the dyebeck, and in order that the rope of cloth does not get entangled, a series of wooden pegs are supplied, in the same way as on the roller washing machines, employed in the bleaching process, only in the case of the dyebeck no revolving roller is provided on the wince. The cloth is of course twisted in the form of a rope.

The dyeing with alizarin can also be performed in an open cistern, similar to those employed in dunging, through which the cloth is passed in full width, when it only takes a few minutes, if a sufficient amount of dyestuff is kept in the bath, and the temperature is kept at the boil.

The Washing.—For the washing of calicoes after the different operations, or the final wash, different machines have been introduced by the different makers, all aiming at perfect washing with minimum water consumption.

In many instances printworks are supplied with a series of machines for doing the necessary set of operations, for instance for goods which have to be raised in bichromate of potash, those which contain chrome yellow, along with black, Prussian blue, &c. The pieces are passed in full width through a series of cisterns, one after another, each supplied with rollers in the interior, and nipping rollers, so that the cloth, after passing through the liquor, is squozen out, and then passed into the next cistern ; for instance, in the first cistern the cloth is passed through bichrome, in the second cistern is washed, in the third soaped, and in the fourth washed again if necessary, and so on until the cloth is passed over the set of drying cylinders at the end of this machine. By supplying several such cisterns the cloth is only passed through the liquor, which is required for its treatment, without passing through the bath, which is not required.

The Soaping —The soaping of the goods is a very important process, for which many arrangements and machines have been devised, one already used for some time (principally the madder styles) being the *soap becks* (Plate XIV.) for continuous soaping, consisting of a set of becks working, on the spiral method, on the system followed in the roller washing machines, being supplied with squeezing rollers, through which the cloth passes after going through the beck. By this arrangement the cloth passes first through one of the machines, and from this to the second, then to the next, &c.

Of recent introductions several machines are working on the cloth spread in full width, and called open soapers or soaping machines. Three of these recent machines, from the respective makers, Mather & Platt's, Gadd's, and Farmer's, are shown in the illustrations (Plates XV., XVI., XVII.). The first of these (Plate XV.) works by the cloth

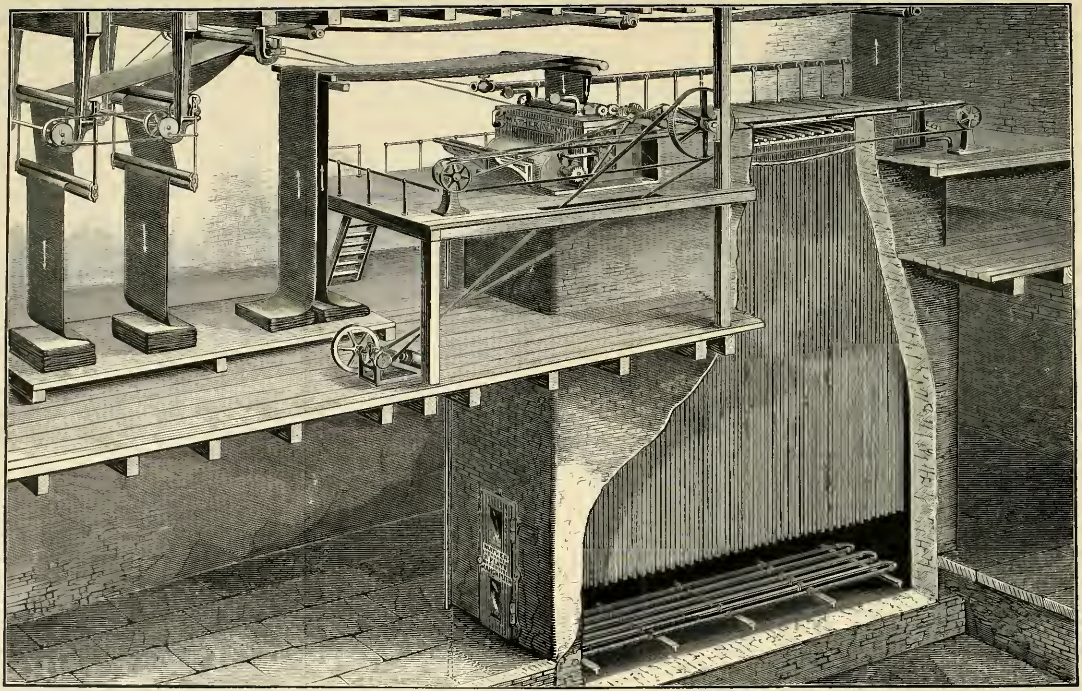


PLATE XIII.–CONTINUOUS STEAMER.

passing over rollers in a series of cisterns, where it is soaped and washed, the loose particles not permanently fixed on the cloth being removed by a system of revolving cylinders, containing broad indiarubber beaters, which act on the whole width of the cloth.

Farmer and Lalance's machine (which is also recommended for other operations of the printworks, even dyeing, fixing, or washing, besides the soaping) treats the cloth also in full width, by forcing it to travel over hollow cylinders, having on their surface a large number of holes, through which, by suitable arrangement, a kind of vacuum or circulation is created, which allows the liquor to pass through the fabric and remove the loose particles; the machine is further supplied with a system of beaters. (Plate XVI.) Gadd's Machine is shown at Plate XVII.

BLEACHING AFTER PRINTING. — In some styles pieces containing much white are bleached at the end, in order to clear the white; this is done by passing the piece through a weak chlorine bath, and then directly through a steaming box, then washed and either dried or starched as the case may be. The pieces are often also slightly blued with ultramarine.

Amongst other appliances of machines of recent introduction our attention has been called to a very ingenious machine for stamping trade marks at the head of grey or bleached cotton pieces, a process which is generally performed by hand by means of a block.

By kind permission of Mr. Thos. Gadd and Mr. Duxbury, the inventor, we have been allowed to see the machine at work.

In concluding this chapter, the author tenders his thanks to the machine makers who have supplied him with information, and enabled him to see some of the machines at work; and those thanks are especially due to Messrs. Mather & Platt, not only for their kindness in supplying numerous blocks and illustrations of their machines and apparatus, but enabling the author, through their influence, to see them at work in printing establishments.

FINISHING PRINTED GOODS.

The finishing of printed cotton fabrics is a very important question, as upon the way the goods have been finished depends, to a great extent, their saleable value. With the exception of Turkey red prints, and some kind of indigoes, all printed goods are subjected to the finishing operations.

The finish varies considerably according to the styles, and especially according to the markets for which the goods are intended; and finishing is a branch of industry which can only be learned by practice, therefore we shall only treat of the principle here, and indicate the apparatus usually employed. For some goods no stiffening is required, while for others a starching all over is necessary; but prints are, as a rule, only starched at the back. In some instances a lustre is required on the cloth, while in others only a matt finish is wanted.

The *starching* of prints all over is performed on the starching machines, and is still in principle the old arrangement of a frame supporting three rollers, one of brass or copper between two of hard wood. The cloth, after passing through a trough, is squeezed by passing between the copper and the wooden rollers to remove the excess of starch; the cloth is then dried on the drying machine, and in order to give smoothness is passed through the mangle or calender. The starch is simply prepared by boiling starch in a pan, often only by direct steam in a tub, and can be made thinner or thicker according to requirements.

Sago flour and potato starch are as a rule preferred by the finisher, but mixtures are found in the market suitable for special purposes. In boiling the starch, a low temperature gives better results than a hard boiling. To impart a more pleasing appearance to goods containing white, a small quantity of blue, principally ultramarine, is added to the starch, and, as a rule, also a softening, such as soap, tallow, &c., and for some purposes glycerine, which is the best material that can be used for the purpose. Often

China clay and other white pigments are added to the starch, in order to give artificial weight and to fill the cloth.

The *back starching* machine is largely used now in the finishing of modern prints; it relies on the principle of a roller revolving in a starch trough, taking up starch on its surface, and giving it to the cloth, which is passed in full width over it. The drying of this back starched cloth is also performed on the cylinders or tins, which are provided with a special arrangement of skeleton wooden cylinders, in order to allow only the surface without the starch to touch the heated cylinder until the starch is sufficiently dry to be passed on the set of cylinders in the ordinary manner, as shown on the illustration of the finishing arrangement (Plate XVIII.), where the starch mangle, back starcher, and drying cylinders are shown, either of the two first being disconnected from the drying arrangement, according to requirements.

The Stretching.—For widening the pieces which have been stretched only in the direction of the length by the different operations of bleaching and printing, several arrangements are devised, working on different principles, such as with grooved cylinders, &c., or on the principle of widening, or as in the so-called *stentering machine*, by the arrangement of a long frame, the widening being performed by means of endless travelling bands containing pins or clamps on both sides of the pieces.

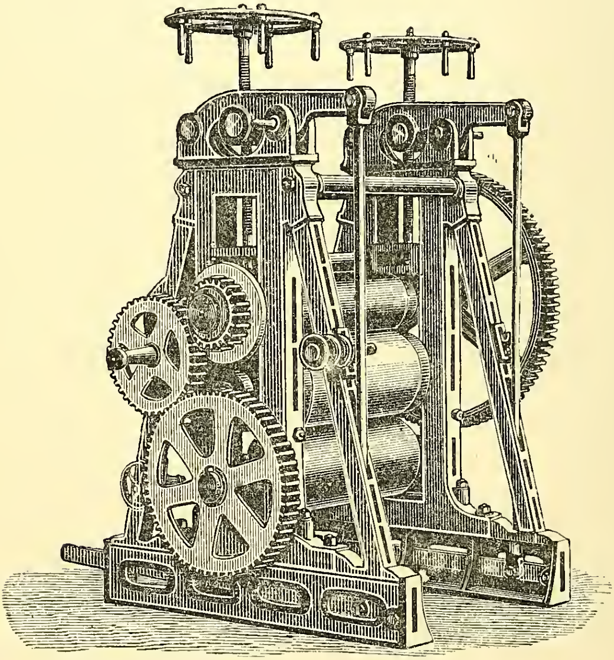
The Calender is of different construction, but it consists in principle of an intermediate iron bowl, and two other bowls, generally made of paper or compressed cotton, and which assert a very heavy pressure on the cloth, which passes round the iron bowl, and consequently between this and consecutively one and the other of the bowls, which assert a heavy pressure on the intermediate iron, one by means of screws or other suitable arrangements.

The iron bowl is generally made hollow, in order that it may be heated by steam, or sometimes by means of heated cannon balls or gas.

The *friction calender or mangle,* which is often required to impart a higher gloss to the goods, works on the principle of two paper bowls, with an iron one at the top, and this latter, besides asserting a heavy pressure on the other two, is made to revolve at a higher speed than they do, and thus a friction is caused on the cloth.

Fig. 13 illustrates a three-bowl friction mangle, by kind permission of Messrs. Bentley and Jackson.

Fig. 13.



Three-Bowl Friction Mangle.

Plate XIX. shows a special calender constructed by Haubold, Junr., Chemnitz.

As stated before, the construction of the calenders varies according to makers and finish required, and machines are also constructed with a larger number of bowls.

ELECTRICITY IN PRINTING.

The application of the electrical current to the production of colouring matters, or for the fixation of dyestuffs in dyeing and calico printing, has attracted considerable attention in the last few years, at the hands of several chemists. It has been known for a long time that aniline black could be produced by electrolysis, but this fact was only considered as a scientific curiosity; it is due principally to the labours and investigations of Prof. Goppelsroeder, that the subject has attained the development at which it now stands. Of course, the application of electricity in dyeing and printing may be considered more as of future than of present possibility; but it is not the first time in the history of scientific chemical or physical industries where industrial application has speedily followed purely scientific discoveries, and consequently we have to await events before we can decide upon the possibility of electricity playing an important part in calico printing.

Prof. Goppelsroeder's discoveries and investigations have been fully recorded in English technical chemical literature, and he has even published, in 1885, a small work in which the different investigations have been fully treated.

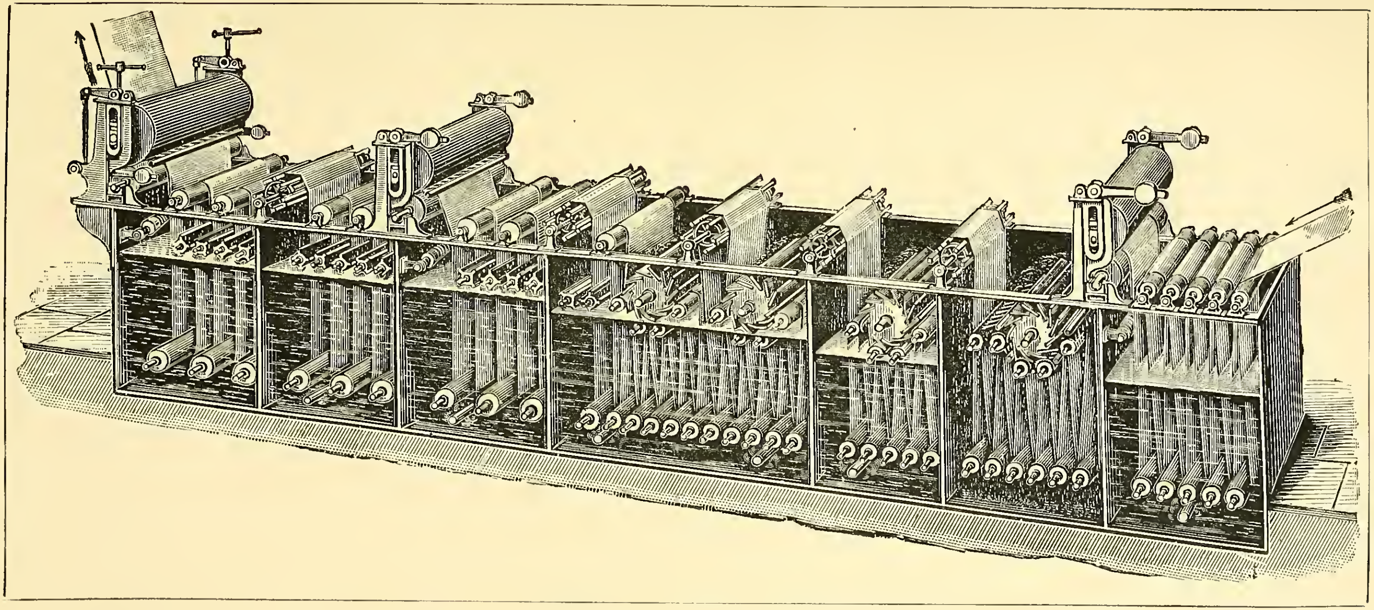
The application of electricity for the developing or fixing colouring matters is based upon the chemical processes largely utilised in printing, *viz.*, oxidation and reduction, and when it is remembered that both processes can be separately effected by the electrical current, we can easily imagine that all the colours which can be produced by oxidation or reduction, ought to be obtained by the electrical process. Consequently we have of the oxidation colours, or of the methods relying on oxidation, the following, which have been fully investigated by Prof. Goppelsroeder:—

aniline black, persulphocyanogen yellow (canarin), the discharge of indigo or Turkey red, and the formation of some colouring matters, such as alizarin from anthraquinone, &c., the bleaching of vegetable fibres and formation of oxycelluiose being also possible by the same process.

In the reduction processes, of course, is included the preparation of an indigo vat for dyeing, and the investigator has also tried to print indigo in a direct way on calico, by utilising the reducing action of the current in the colour box. He has also aimed at producing an electrical printing machine, by which colours could be fixed on calico by the electrolitic direct process, but, as said before, we must wait awhile before we can pass any judgment over the feasibility of electrical application in calico printing.

So far, however, electricity has been utilised in calico printing, but in a different manner, for the galvanoplastic processes, and depositing either copper on iron shell rollers, thus producing printing rollers with a copper layer at a very low cost; or for the commonly called galvanising process, by coating the ordinary copper rollers with a thin layer of nickel, in order to render them more liable to stand acid colours. The gilding of copper rollers has scarcely ever been employed, but considering the low cost of depositing a very thin film of gold, which can be done by the modern galvanoplastic process, it is a matter well worth trying for those rollers which are used for printing very acid colours.

The application of electricity in an indirect way in calico printing establishments, for the production of electric light, is a matter too well known to deserve any special mention here. By the electric light the colours appear as well as by day-light, which is not the case with the gas light, and printers are therefore enabled to judge well of the colours they have produced, when no day-light is available.



XV.—MATHER & PLATT'S OPEN SOAPING MACHINE.

PRINTING WOOLLEN FABRICS.

The following particulars are due to the kindness of Mr. Horace Koechlin, of Lörrach, to whom are also due the patterns of printed woollen fabrics at the end of this work. The process for the printing of wool fabrics is as follows:— The goods are previously scoured in the usual way, by taking all the precautions necessary to the treatment of fine woollen materials, and are afterwards bleached.

The bleaching is now principally effected by means of peroxide of hydrogen or oxigenated water, followed by a treatment in bisulphite of soda. The bath of the hydrogen peroxide (commonly called here hydroxyl) is prepared by diluting the commercial product (at 12 volumes) with 2 to 10 parts of water, according to the nature of the goods and the whiteness required, light goods needing only a moderately strong bath, while heavy thick goods require a more concentrated one. The goods after passing through this bath are wound on a roller and left there for 24 hours; they are then washed and afterwards passed through a bisulphite of soda bath, prepared with bisulphite at 35° Bé., diluted with 2 to 10 times its volume of water. The cloth is again rolled on the roller, left there for 24 hours, and then removed and dried. When both the baths of oxygenated water and bisulphite have been taken sufficiently concentrated, the first containing one half and the second one-third of the original product diluted in water, then a white is produced as fine as that obtained on cotton. By this new method of bleaching a better white results than can be obtained by the older method with sulphurous acid.

Before printing, the goods have to undergo a very important operation, without which no satisfactory results can be obtained. They must be treated by means of sodium hypochlorite solution, in which the pieces are passed in full width, in a vat containing a weak solution of the latter, acidulated with sulphuric acid.* Great care must be taken in preparing this chlorine bath; the more concentrated it is the better is the result, so far as the colours are concerned, but there is a limit in the possible strength, since if the bath be too strong the goods acquire a yellowish tinge, and also become harsh to the feel. After washing, the pieces are dried and are ready for printing. The preparation of the colours for this purpose does not offer any special difficulty, and the methods have been well described in Crooke's works, to which those interested in the subject would do well to refer. Coal tar colours are now employed in increased quantities, since many of the acid colours display such resistance to the action of light as to leave nothing to be desired in this respect. In the preparation of the printing colours, gum is generally used as thickening, and to this is added a solution of the colouring matter, generally with acetic acid, and afterwards with an addition of glycerine. The colours are fixed by steaming, and very often the cloth is prepared with tin mordants before printing. Rose shades are mostly produced by means of the eosines which, although not fast against light, give such shades as to stand unrivalled. Dark blues are produced with the induline preparation of the Höchst Colour Works, the product mentioned in another part of this work. Roccelline, the azo scarlets, oranges, etc., are also pretty largely employed for wool printing, and to a certain extent, of course, also the older basic aniline colours.

Before printing, the pieces must be moistened by hanging them in a damp stove or rolling them up in a damp cloth, care of course being taken that they do not get too wet,

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* The chlorination of the wool or half-wool pieces before printing was first introduced into practice in this country by John Mercer, to whom are due also many other improvements in calico printing and in the printing of fabrics generally, as clearly appears from the accounts of his life, contained in the book lately published by Parnell.

otherwise the colours would run during the steaming, which lasts one hour.

The following recipe for black is also due to Mr. Koechlin's kindness:—

Printing Black on Woollen Fabrics with Di-nitrosoresorcine.

100 grs. di-nitrosoresorcine paste	1lb.
250 grs. acetic acid	¼ gal.
750 grs. tragacanth water	¾ gal.
50 grs. red prussiate	½lb.
250 grs. gallocyanine paste	2½lbs.

Steam one hour and wash.

The following may also be found interesting:—

Printing Colours for Woollen Goods.

The cloth is scoured and bleached, then washed. Next follows for half an hour a bath of stannous chloride at 33° Tw., then a sulphuric acid bath at about 1° Tw. for 15 minutes, the cloth being afterwards well washed, dried, and pressed.

Red.

100 cc. water	1 gal.
10 cc. starch	1lb.
25 cc. dextrin	2½lbs.

Boil, then add

5 grs. fast red (azo scarlet) BB	8oz.

Stir until dissolved, and when almost cold add

1½ grs. oxalic acid	2½oz.

Stir until cold and print.

Blue.

100 grs. water	1 gal.
10 grs. starch	1lb.
25 grs. dextrin	2½lbs.

Boil, then add

2½ grs. solid tin chloride	4oz.
3½ grs. fast blue for wool	5½oz.

Stir until cold.

Yellow.

100 grs. water	1 gal.
10 grs. starch	1lb.
25 grs. dextrin	2½lbs.

Boil, then add

12½ grs. acetic acid	1¼lbs.
3½ grs. orange or yellow coal-tar colour for wool	5½oz.

After printing hang up in a warm room over night; afterwards roll up with linen cloth and steam for one hour; then leave to hang up in the air for 24 hours, wash and dry in the shade.

Printing with Fast Violet on Woollen Goods Dyed with Xylindin Scarlet 3R.

Ed. Kopp recommends the following process:

The dyeing is performed in the usual way with the colouring matter and sulphuric acid and Glauber salt by beginning at about 55° C. and going up to about 90° C in one hour. The dyed cloth is then rolled up and passed twice through the damping machine, then printed on the machine with a roller deeply engraved, but without heavy pressure. The blue colour is prepared as follows:

8 litres gum water (1 : 1).
2 litres solid violet (the bisulphite combination as below).
1·280 grs. acetic acid.
1·280 grs. tin crystals.

Solid Violet S (bisulphite combination).

1 litre solid violet (Durand and Huguenin's).
30 grs. bisulphite of soda 35° Bé.

Leave to react for 24 hours, and keep in closed bottles for use. After printing, the cloth is rolled up in a damp back

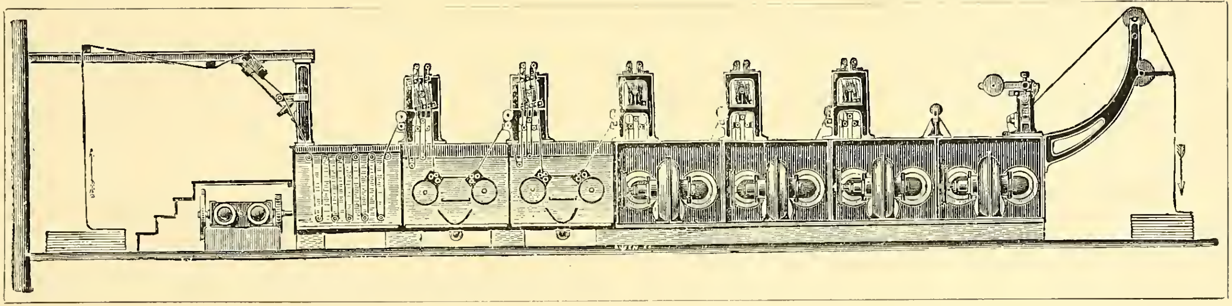


PLATE XVI.—FARMER AND LALANCE'S OPEN SOAPER.

cloth, and left rolled up for one hour, then steamed for one hour without pressure. The cloth is afterwards washed in running water to develope the blue, then washed ten minutes in the washing machine, and dried.

Koechlin also obtains red and blue prints by means of indophenol blue printed on cloth dyed with azo scarlet.

COMPARATIVE HYDROMETER SCALE:

Sp. Gr. Beaumé and Twaddle.

Sp. Gr.	Beaumé.	Twaddle.
1·000	0 deg	9deg.
1·007	1 ,,	1·4 ,,
1·014	2 ,,	2·8 ,,
1·022	3 ,,	4·4 ,,
1·029	4 ,,	5·8 ,,
1·036	5 ,,	7·2 ,,
1·044	6 ,,	8·8 ,,
1·052	7 ,,	10·4 ,,
1·060	8 ,,	12·0 ,,
1·067	9 ,,	13·4 ,,
1·075	10 ,,	15·0 ,,
1·083	11 ,,	16·6 ,,
1·091	12 ,,	18·2 ,,
1·100	13 ,,	20·0 ,,
1·108	14 ,,	21·6 ,,
1·116	15 ,,	23·2 ,,
1·125	16 ,,	25·0 ,,
1·134	17 ,,	26·8 ,,
1·143	18 ,,	28·6 ,,
1·152	19 ,,	30·4 ,,
1·161	20 ,,	32·2 ,,
1·171	21 ,,	34·2 ,,
1·180	22 ,,	36·0 ,,
1·190	23 ,,	28·0 ,,
1·199	24 ,,	39·0 ,,
1·210	25 ,,	42·0 ,,
1·221	26deg	44·2deg.
1·231	27 ,,	46·2 ,,
1·242	28 ,,	48·4 ,,
1·252	29 ,,	50·4 ,,
1·261	30 ,,	52·2 ,,
1·275	31 ,,	55·0 ,,
1·286	32 ,,	57·2 ,,
1·298	33 ,,	59·6 ,,
1·309	34 ,,	61·8 ,,
1·321	35 ,,	64·2 ,,
1·334	36 ,,	66·8 ,,
1·346	37 ,,	69·2 ,,
1·359	38 ,,	71·8 ,,
1·372	39 ,,	74·4 ,,
1·384	40 ,,	76·8 ,,
1·398	41 ,,	79·6 ,,
1·412	42 ,,	82·4 ,,
1·426	43 ,,	85·2 ,,
1·440	44 ,,	88·0 ,,
1,454	45 ,,	90·8 ,,
1·470	46 ,,	94·0 ,,
1·485	47 ,,	97·0 ,,
1·501	48 ,,	100·2 ,,
1·516	49 ,,	103·2 ,,
1·532	50 ,,	106·4 ,,

THE PRINCIPAL STYLES OF CALICO PRINTING, 1886.

PRINTED (DIRECT) COLOURS.

I.—STEAM OR EXTRACT STYLES.

(a) Coal Tar Colours.

Alizarin.—Reds, Pinks, Purples, Chocolates, Browns, &c. Galloflavine Yellow, Anthracene Blue, Orange, Anthracene Brown, Galleine Violet, Cerulein Olive, Gallocyanine Violet, Dinitroso-Resorcin Olive.

Basic Aniline Colours.—Magenta and Safranine Reds, Aniline Blues (prepared paste colours), Methyl Violets, Methyl and Direct Greens (Malachite, &c.), Methylene and Aethylene Blues, Auramine Yellow, Victoria Blue, Induline Paste.

Acid Colours.—Soluble Aniline Blues, Azo Colours, Eosines.

(b) Dyewood Extracts (*Natural Organic Colouring Matters.*)

Logwood.—Blacks, Purples, Olives, Browns, &c.

Quercitron Bark.—Yellow, Orange, Combinations.

Sapan and other Red woods.—Red, Pink, Brown, Chocolates, &c.

Catechu.—Browns and Combinations.

Annatto.

Cochineal.—Pinks, Reds, Scarlets.

(c) Steam Mineral Colours.

Prussiate Blues, Chrome Yellow, Cadmium Yellow, Chrome Orange, Canarin (Persulphocyanogen) Yellow, Manganese Brown, Copper Phosphate Green.

II.—PIGMENT STYLES *(Fixed by Albumen).*

Vermilion Red, Ultramarine Blue, Chrome Green, Chrome Yellow, Chrome Orange, Olives, Browns, Buffs, Chocolates, Blacks, &c.

III.—OXIDATION COLOURS.

Aniline Black, Naphtylamine Puces and Greys, Phenylen and Toluylen Diamine Browns or Bronzes, Persulphocyanogen Yellow, Colours with Amines on Manganese Brown, Buffs, Cutch Colours, &c., Colours requiring Chroming for their development.

IV.—DIRECT INDIGO PRINTING.

Alkaline Styles.

China Blues, &c.

Artificial Indigo.

Glucose Process.—Blue and Red, and other possible combinations.

Alkaline Mordants.—Annatto.

DYED COLOURS.

V.—ALIZARIN DYED STYLES.

Old Madder Styles *(Dyed on Printed Mordants, either Alumina or Iron, or mixtures of both).*

Reds, Pinks, Browns, Purples, Chocolates, Blacks.

Modifications of Alizarin Dyed Styles.
- *Reserved Styles.*
- *Padding Styles.*
- Dyeing with Dyewood or Coal Tar Colours on printed or padded Mordants.

VI.—TURKEY RED STYLES *with Discharge.*

White, Yellow, Blue, Green, Black, on Red ground.

VII.—INDIGO STYLES *Dipped in the Vat. Designs produced by resist or discharge.*

White, Yellow, Orange, Green, Red, Olive, &c., on Blue ground.

VIII.—MANGANESE BRONZE STYLES.

White, Yellow, Blue, Green, Red, Black, on Bronze ground.

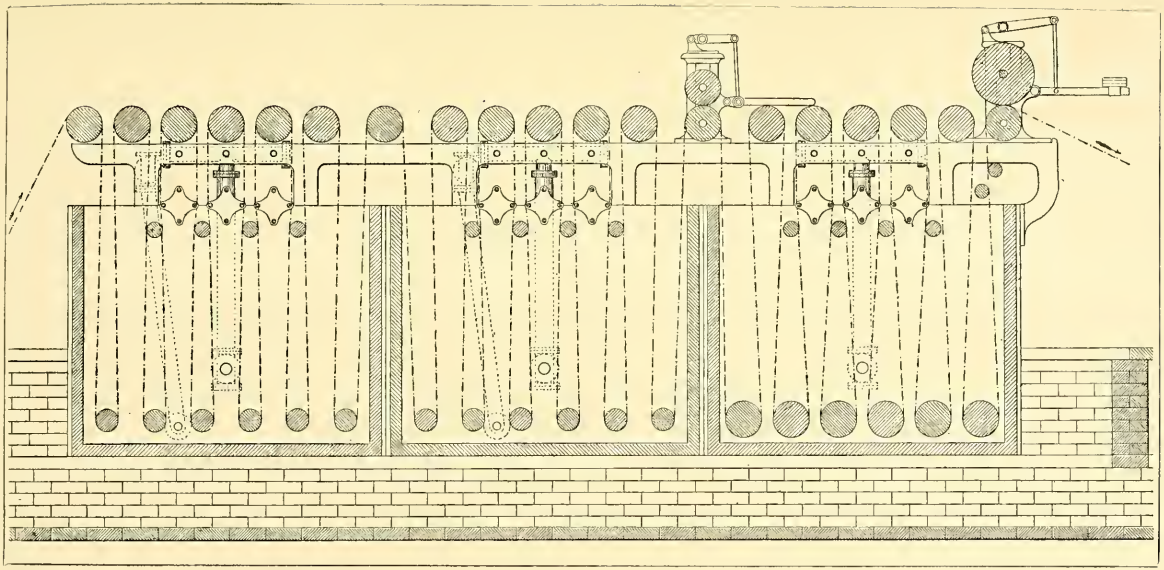


PLATE XVII.—GADD'S OPEN SOAPER.

EXPLANATIONS TO PRINTED PATTERNS.

Plate 1.

Nos. 1 and 3 have been printed with *black lake* by means of albumen (pigment styles).

No. 2, *gold* or *bronze powder* on cream ground. These patterns are due to the kindness of Messrs. Alfred H. Midwood and Co., of Fountain Street, Manchester, who have had them printed purposely for this work.

Plate II.

The three patterns on Plate II, illustrating the *Turkey red styles,* I owe to the kindness of Mr. Kerr, of Messrs. Steiner and Co., Turkey Red Dyers and Printers, Church.

Plate III.

For Nos. 7, 9 and 11, illustrating some steam coal tar colours, I am indebted to Messrs. Grafton and Co.

Nos. 8, 10 and 12 are Mulhouse's production of the firm of Dollfus, Mieg and Co., whom I have also to thank for their previous kindness in supplying me with patterns to illustrate the production of different articles of prints, &c.

No. 8—*Indigo print* produced by the discharging method.

No. 10—*Steam colours,* the red being alizarin, and the cloth afterwards padded over with "*crême à l'ochre*" (pigment buff), fixed with albumen.

No. 12—*Light pink* and *white reserve,* padded over with steam alizarin pink.

The same firm had also sent me a splendid pattern, representing a flower on light blue ground (the latter produced with alizarin blue), to illustrate some of the effects obtained by steam colours, but unfortunately it could not be inserted, as by cutting up in small bits it would have lost all its effect by being too much mutilated.

Plate IV.

Nos. 13, 15, 17, and 18, are due to Mr. Horace Koechlin, whose generosity and kindness in supplying me with patterns, information, and even recipes, have been very great.

No. 13 illustrates the discharging of *indigo dipped goods* and fixation of pigment colour at the same time.

No. 15 is produced by the *direct indigo printing,* glucose process, on Turkey red dyed cloth.

No. 16 has been produced with gallocyanine (steam).

No. 18 is dyed dinitrosoresorcine olive, discharged with stannous chloride, as for manganese bronze.

For the patterns Nos. 14 and 16 I am indebted to the kindness of Messrs. Salis Schwabe and Co., and to these gentlemen, and to their manager, Mr. Scott, I am obliged for permission to visit their well appointed and extensive works at Rhodes, and for much valuable explanation and information concerning the printing processes. Pattern No. 31 is also due to them.

No. 14 is natural indigo printed on Turkey red cloth by the glucose process.

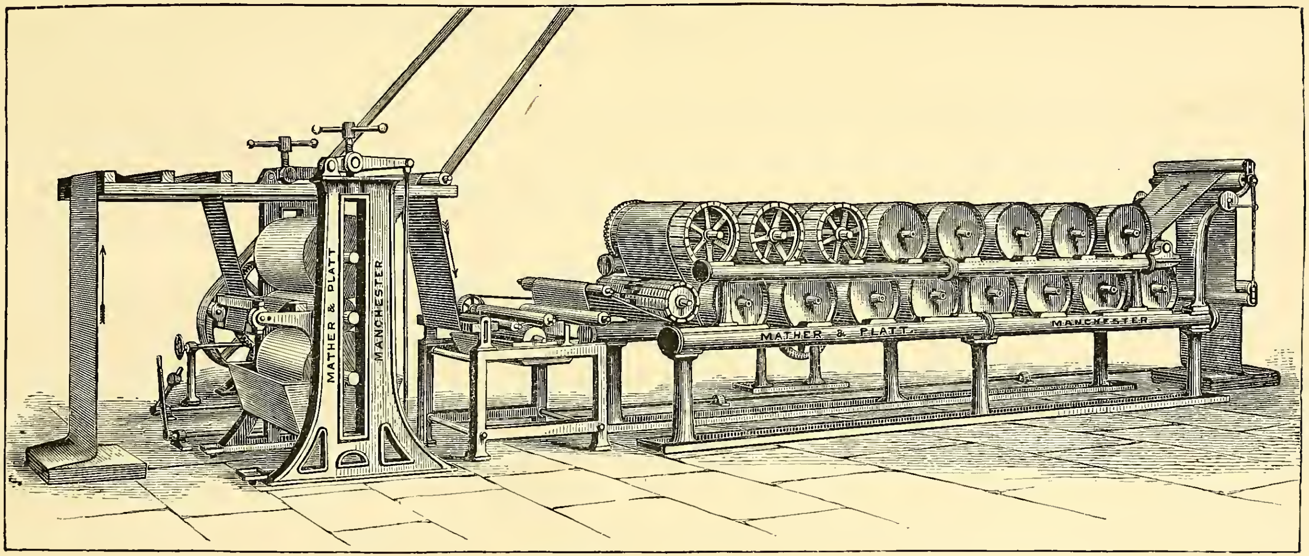
No. 16 illustrates the production of coloured discharges, by means of the chromic acid process for the fixation of pigments with albumen.

Plate V.

No. 19 is steam *azarine* pink, for which I am obliged to Mr. Liebermann, the Manchester agent of the Höchst Colour Works.

No. 20 — *Indigene* blue of the Elberfield Colour Works, kindly supplied by their Manchester agents, Messrs. Bryce and Rumpf.

PLATE XVIII.—FINISHING MACHINE.



Nos. 21, 22, 23, 24, 25, 29, 30, 34 and 36 are due to Mr. Horace Koechlin, with the corresponding information.

No. 21—Steam colours, the blue being a mixture of *alizarin blue* with *gallocyanine,* fixed with acetate of chrome.

No. 22—Discharge on light indigo, by the red prussiate process. *White* with red prussiate and chalk.

Red—Alizarin lake fixed by albumen, along with red prussiate and chalk or carbonate of magnesia.

Yellow—Chrome yellow with albumen and red prussiate and chalk.

Olive—Ceruleine fixed with acetate of chrome, the shade being modified by means of Persian berry extract.

Mr. Koechlin states on this occasion, that the method which has been recommended some years ago by Depierre, had been given up on account of its irregularity; by many trials he has, however, found that this irregularity is due to the reduction of the red prussiate by means of albumen, and to remedy this he recommends the addition of an oxidizer to the colour, and for this purpose employs chlorate of potash in the proportion of 50 grs. per litre. By this process a discharge can be effected even on pretty deep blues.

No. 23—The blue is *indophenol* printed on cloth dyed with *benzopurpurin.*

No. 24—*Dinitroso resorcine olive* fixed by steaming with nitrate of iron. Although by dyeing the fixation of this dyestuff requires a very strong iron mordant, the contrary is the fact in printing; as $^1/_{64}$ litre of nitrate of iron at 50° Bé. is sufficient for 100 grs. of dinitroso resorcine. The colour produced is fast.

PLATE VI.

No. 25—Steam colours, the ground being a mixture of alizarin, Persian berry extract and gallocyanine fixed by means of acetate of chrome; the gallocyanine is preferred to logwood on account of its being faster, and allowing the colours to keep better.

No. 26—*Alizarin purple* style: *red* alumina mordant thickened and mixed with tin salt to reserve the purple.

White—Citrate of soda.

Black—Iron with logwood.

Chocolate—Alumina and iron.

Purple—Padded all over, being weak iron liquor simply thickened with starch paste.

After printing, pieces are aged, dunged, and dyed in alizarin. This pattern has been printed at Messrs. Ashton and Co.'s, Newton Bank Printworks, Hyde, where also the patterns 32, 33, and 35 have been purposely printed for this work. I must express my thanks to these gentlemen and to their manager, Mr. Schmidlin, to whom also the particulars concerning the production of the patterns are due, and much useful information concerning the printing processes and machinery.

No. 27—*Aniline black* ground on *benzopurpurin* dyed cloth, for which I am indebted to my young friend and pupil, Mr. W. Melland, who has had it printed for me at Messrs. C. H. Midwood and Co.'s Works, Ardwick.

No. 28—*Induline paste* blue, of the Hôchst Colour Works, with steam alizarin red.

No. 29—Light indigo ground. The dark blue is *indophenol* printed at the same time as the white discharge, which is produced by red prussiate and chalk. After steaming, a chroming is necessary in order to reoxidize the indophenol.

No. 30—Indigo ground. *Yellow*: Chrome yellow with albumen + neutral chromate.

White—Neutral chromate.

Black—Aniline black.

Discharge effected by means of oxalic acid.

Plate VII.

No. 31—Aniline black and dyed alizarin red.

No. 32—*Phenylen diamine* brown or bronze.

No. 33—*Natural indigo* printed by the glucose process.

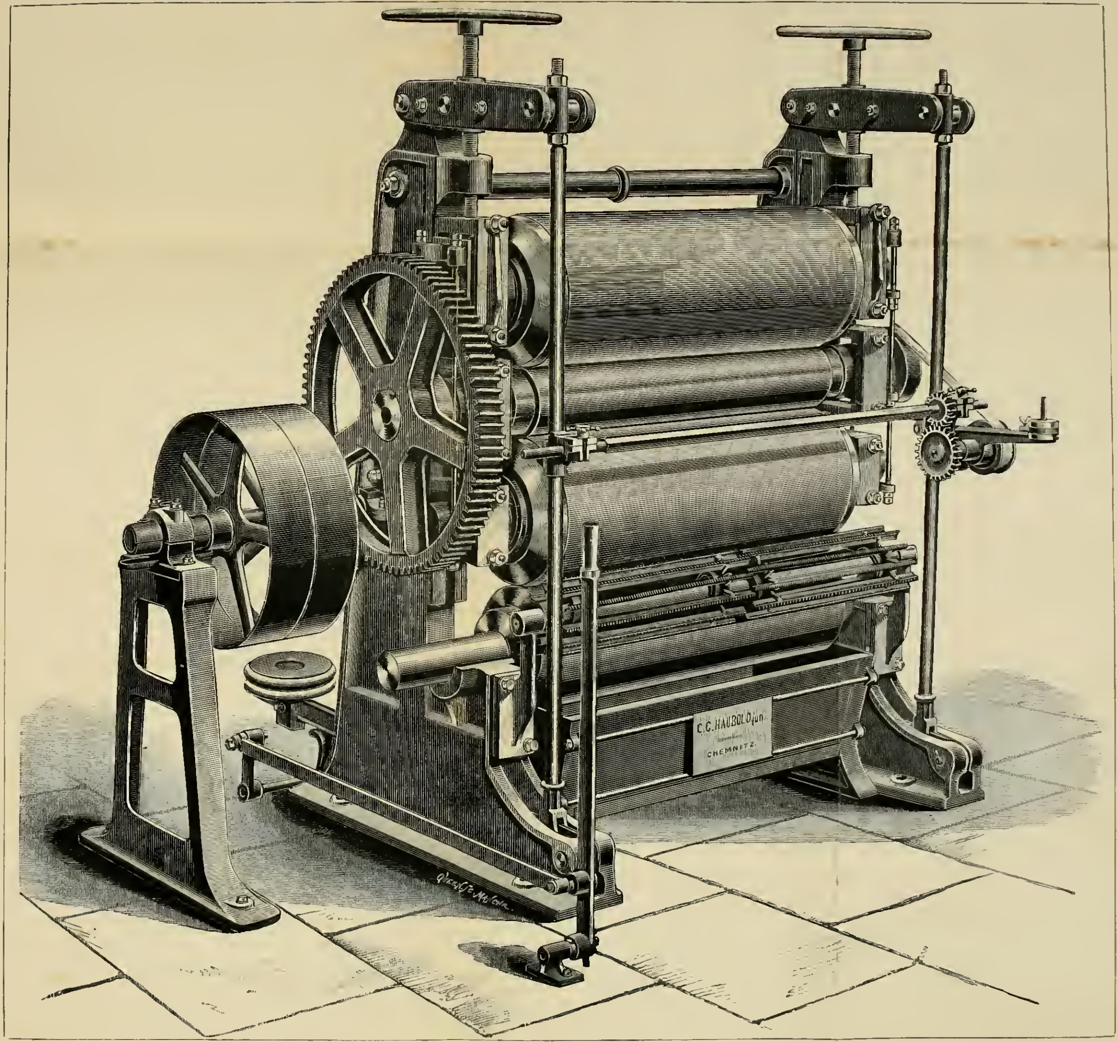


PLATE XIX.–CALENDER

No. 34—Steam colours. Ground mixture of alizarin, Persian berry extract, gallocyanine and acetate of chrome, same as pattern 25, but with a smaller amount of gallocyanine.

No. 35—*Manganese bronze style.*

Red—Eosine thickened with starch paste and fixed with tannic acid; colour contains tin salt to discharge the bronze. Precipitate of tannic acid and tin salt is soluble in the excess of the latter.

Yellow—Chromate of lead pulp thickened with starch containing the necessary amount of tin salt.

No. 36—Mordanted with chromium alkaline mordant (Koechlin's method); dyed with *gallocyanine* and *bark.*

PLATE VIII.

Patterns due to Mr. Horace Koechlin (Koechlin-Baumgarten, Lörrach). For these the reader is referred to the chapter on the Printing of Woollen Fabrics.

Pattern 38—Gallocyanine and indo-phenol on wool previously dyed with xylidin scarlet.

No. 39—Dinitroso resorcine black.

No. 40—Dark blue ground produced with blue paste of the Höchst Colour Works.

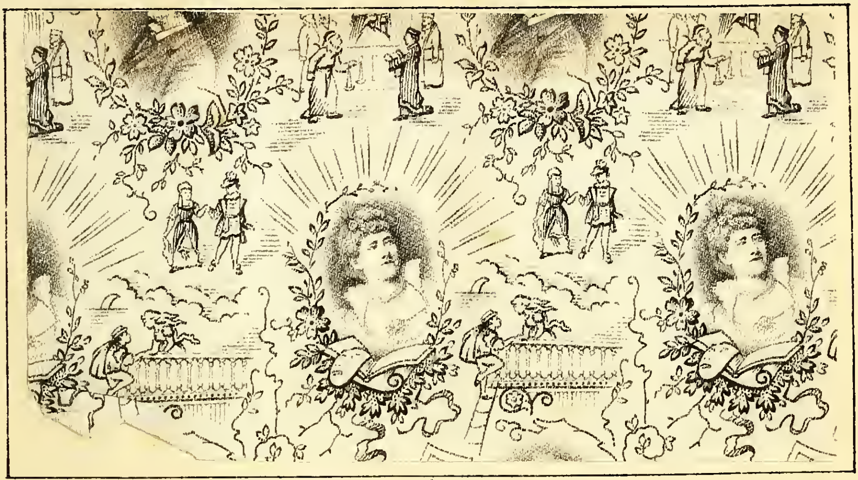
No. 41—Cloth dyed with xylidin scarlet printed on with gallocyanine and Persian berry extract, tin oxide and carbonate of soda.

Before concluding I must also express my thanks to Mr. Schad, the agent for the Berlin Aniline Colour Works, for patterns and dyestuffs supplied to me on different occasions.

I must also express my regret that patterns illustrating *alizarin blue* and *auramine yellow,* kindly supplied to me by Messrs. Schott, Segner and Co., the agents of the Badische Anilin and Soda Fabrik, who had them printed on purpose for me, have not been inserted for want of room; the same fate has been shared by other patterns supplied by other firms.

I am very thankful for the great kindness shown to me on this and other occasions by all those gentlemen to whom I have applied, either for patterns or information.

I



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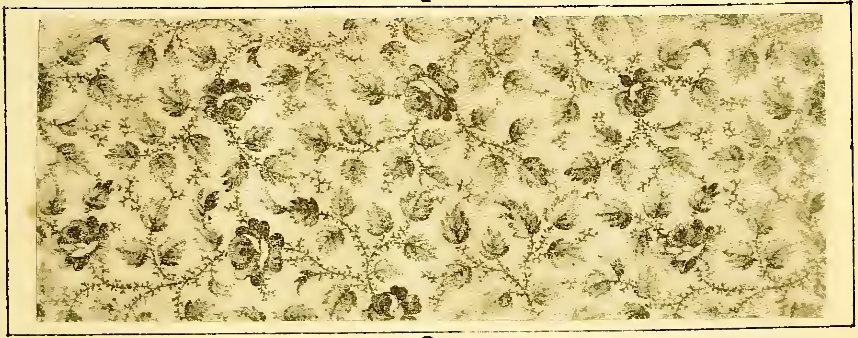

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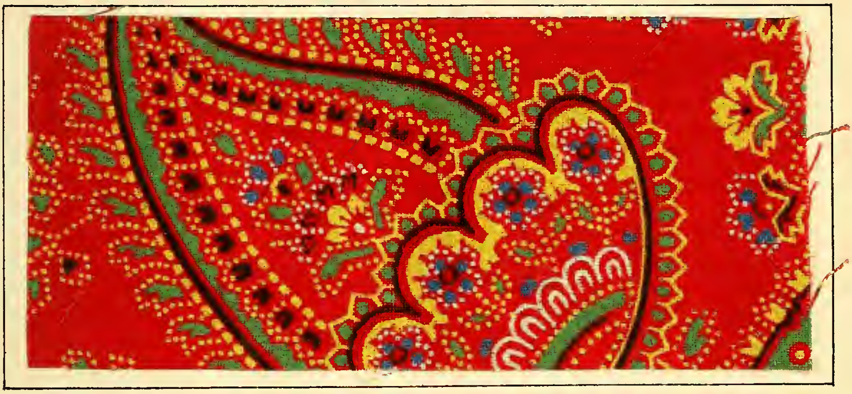

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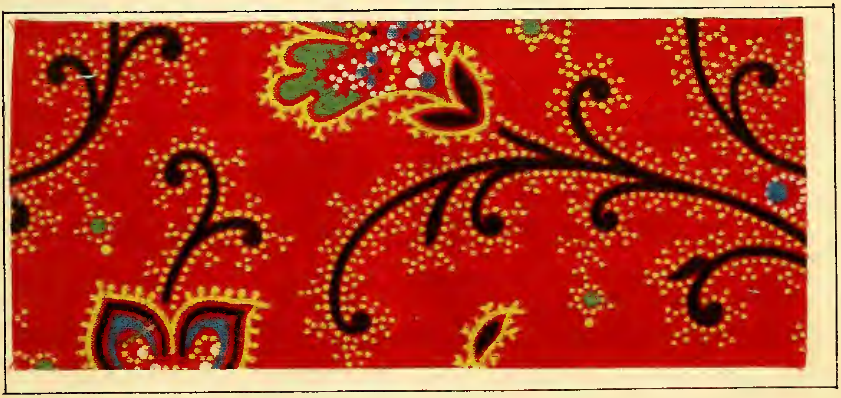

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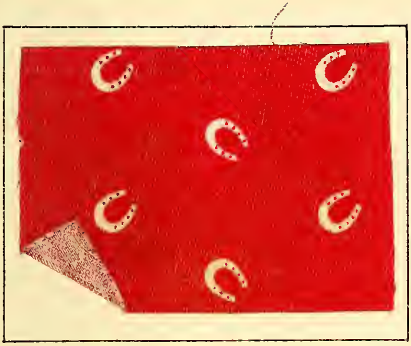

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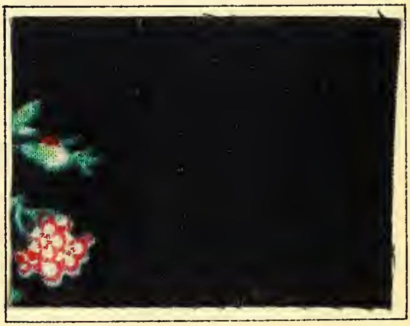

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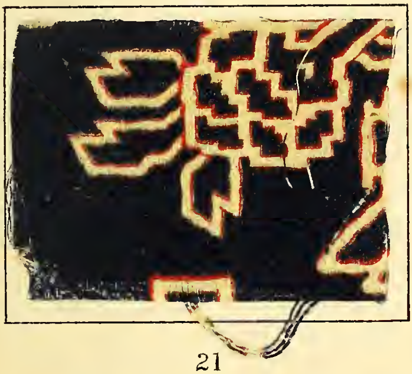

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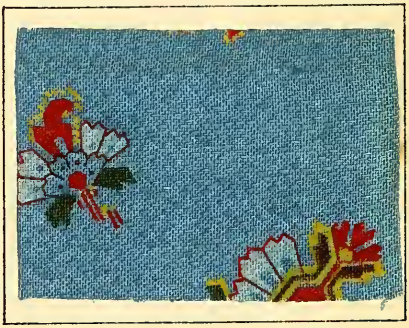

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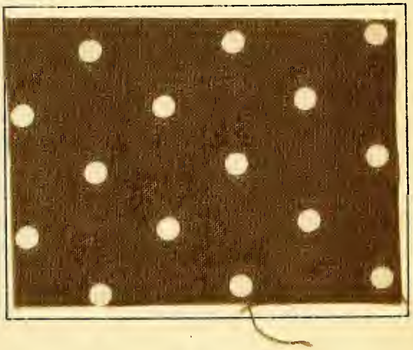

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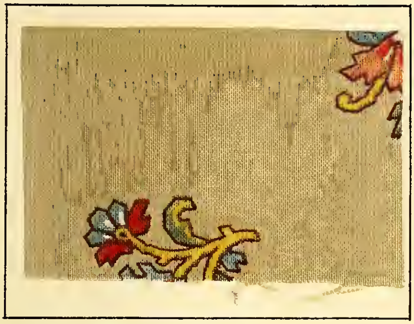

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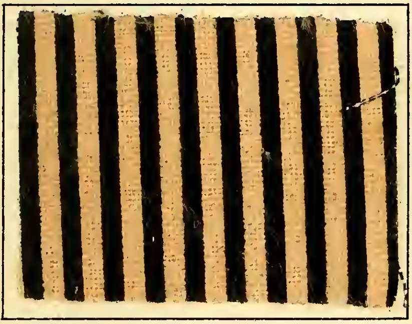

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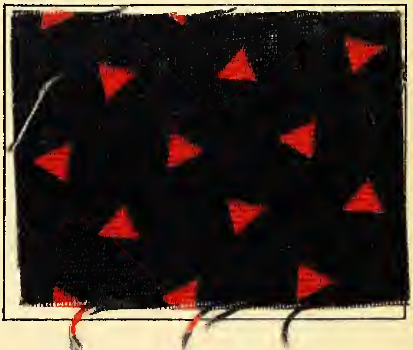

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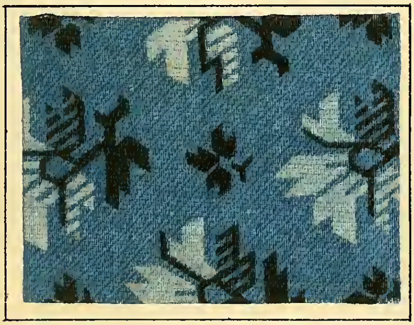

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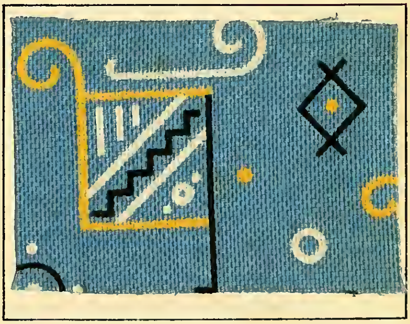

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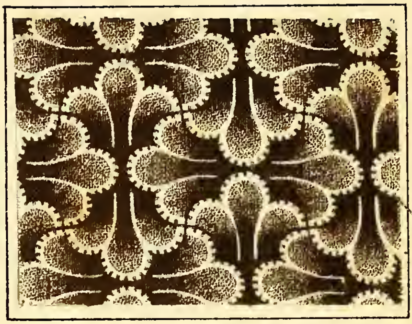

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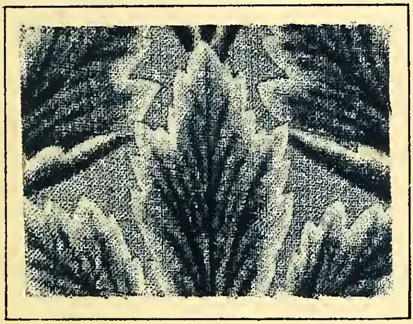

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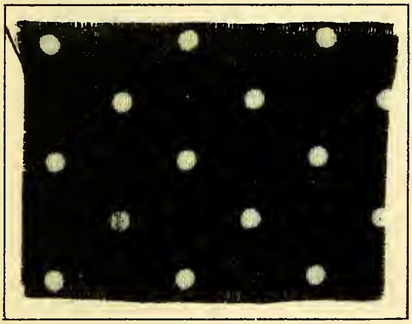

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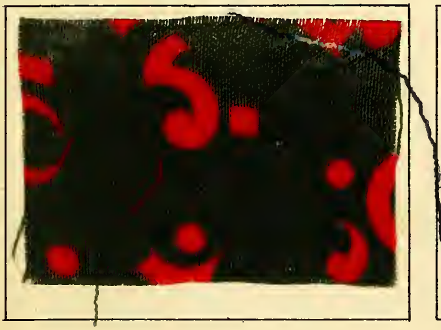

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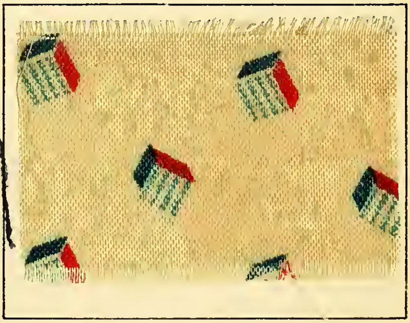

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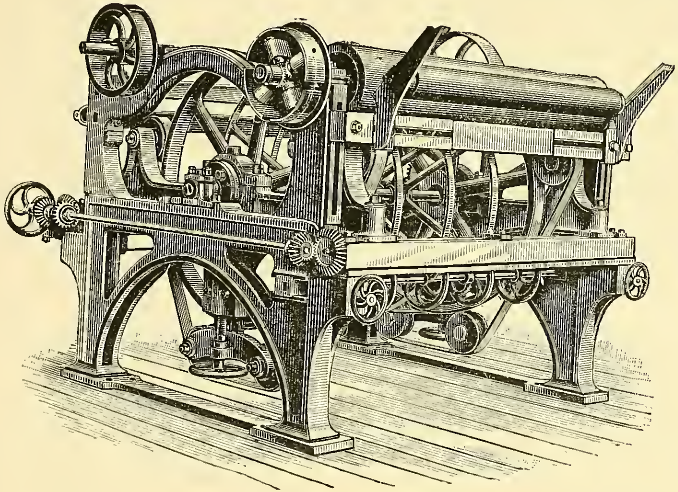

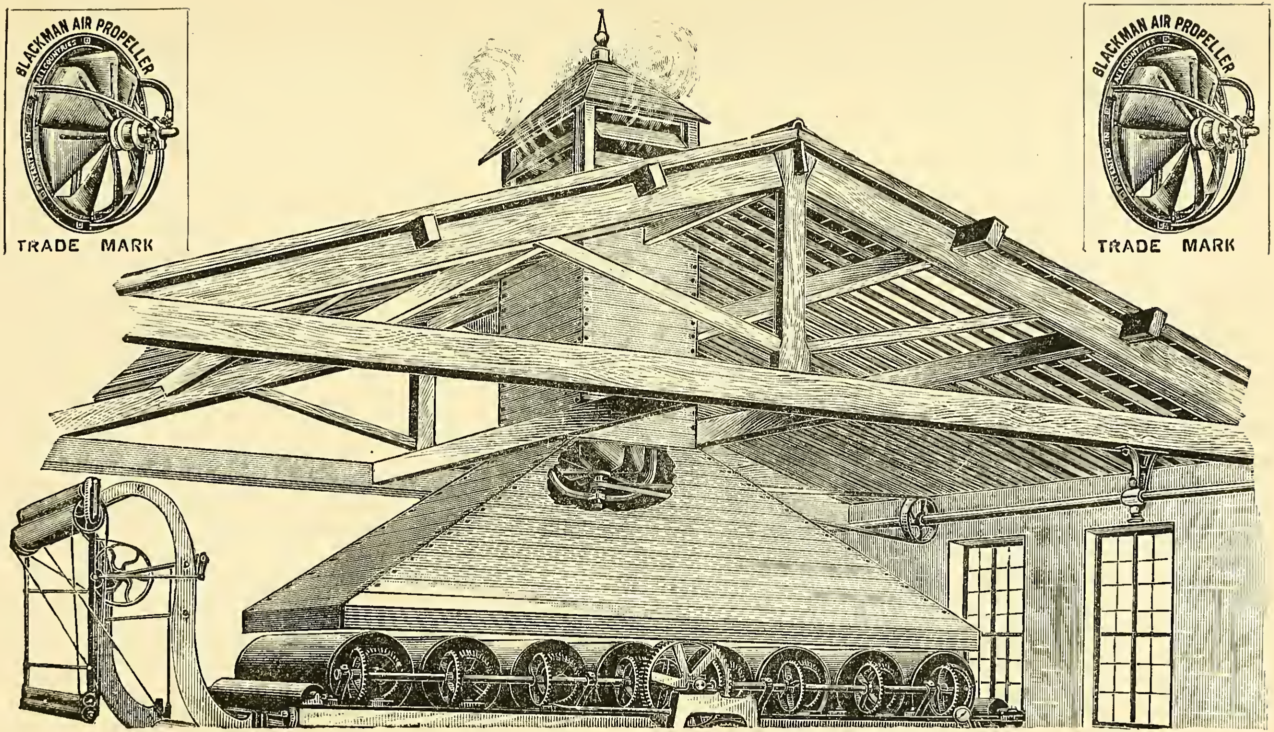

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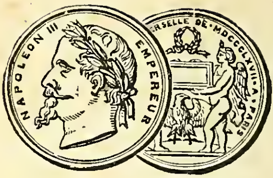

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