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DYEING

AND

CALICO-PRINTING.

BY

EDWARD ANDREW PARNELL,

AUTHOR OF

"ELEMENTS OF CHEMICAL ANALYSIS."

REPRINTED FROM

Parnell's "Applied Chemistry in Manufactures, Arts, and Domestic Economy," 1844.

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In many parts of the article on Calico-printing, I have derived material assistance from my esteemed friend Mr. Mercer, of the Oakenshaw print-works, near Blackburn, to whom I feel myself bound to return my sincere thanks. I am also desirous of expressing my obligations to Mr. John Graham of the Mayfield print-works, Manchester; and to Mr. James Hindle of the Sabden works, near Whalley.

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DYEING AND CALICO-PRINTING.

DYEING AND CALICO-PRINTING.*

§ I. History of Dyeing and Calico-printing.—II. General Properties of Vegetable Colouring Matters.—III. General Nature of Dyeing Processes.—IV. Calico-printing Processes.

In the various operations of dyeing and calico-printing are exhibited some of the most refined and ingenious applications of chemical science. Though many processes in these arts were practised for ages before any just views were entertained of the chemical nature of tinctorial substances, yet dyeing is strictly a chemical art, and it cannot be properly understood without some acquaintance with the chemical properties of the acting bodies.

The great object of all dyeing operations is the impregnation of a textile fabric with coloured substances derived from animals, vegetables, and minerals, in such a manner as to render them incapable of being removed by washing with water. The modes of effecting this object vary as greatly as the colouring matters differ from each other in their chemical habitudes. Though the chemical reactions which are exhibited in the various dyeing and print-

* For a considerable portion of the materials from which the present article is compiled, I am indebted to Mr. Mercer, of the Oakenshaw print-works, near Blackburn, and to Mr. John Graham, of the Mayfield print-works, Manchester.

ing processes are, for the most part, sufficiently intelligible, yet they are sometimes of a highly complex character; and the theoretical principles of a few valuable processes, discovered accidentally, are even yet but imperfectly understood.

§ I. HISTORY OF DYEING AND CALICO-PRINTING.

In the East Indies, in Persia, in Egypt, and in Syria, the art of dyeing has been successfully practised from time immemorial. In the books of the Pentateuch frequent mention is made of linen cloths dyed blue, purple, and scarlet, and of rams' skins dyed red; and the works of the tabernacle, and the vestments of the high-priest, were enjoined to be of purple.

The place of antiquity where dyeing was most extensively carried on, as the general business of the inhabitants, was probably Tyre, the opulence of which city seems to have proceeded in a great measure from the sale of its rich and durable purple. This colour was prized so highly, that in the time of Augustus a pound of wool dyed with that material cost, at Rome, a sum nearly equal to thirty pounds of our money. The Tyrian purple is now generally believed to have been derived from two different kinds of shell-fish, described by Pliny under the names *purpura* and *buccinum*, and was extracted from a particular organ in their throats to the amount of one drop from each fish. It is at first a colourless liquid, but by exposure to air and light become successively citron-yellow, green, azure, red, and, in the course of forty-eight hours, a brilliant purple. If the liquid is evaporated to dryness soon after being collected, the residue does not become coloured in this manner. The purple is remarkable for its durability; it resists the action even of caustic alkalies and most acids. Plutarch observes, in his Life of Alexander, that, at the taking of Susa, the Greeks found in the royal treasury of Darius a quantity of purple stuffs of the value of five thousand talents, which still retained its beauty, though it had lain there for one hundred and ninety years. The properties of the colouring juices of shell-fish have been investigated by Cole, Gage, Plumier, Duhamel, and Reaumur, who have succeeded in procuring a purple dye, though inferior to what may be obtained by other dye-stuffs.

It does not appear that the art of dyeing was much cultivated in ancient Greece. In Rome it received a little more attention; but very little is now known of the processes followed by the Roman dyers, such arts being held, by them, in too little estimation to be considered worth describing. The principal ingredients used by the Romans were the following:—of vegetable matters,—alkanet, archil, broom, madder, nutgalls, woad, and the seeds of pomegranate and of an Egyptian acacia: of mineral productions,—copperas, blue vitriol, and a native alum mixed with copperas.

The progress of dyeing, as of all other arts, was completely arrested in Europe, for a considerable time, by the invasion of the northern barbarians in the fifth century. In the East the art still continued to flourish, but it did not revive in Europe until towards the end of the twelfth, or the beginning of the thirteenth century. One of the principal places where dying was then practised was Florence, where it is said there were no less than two hundred dyeing establishments at work in the early part of the fourteenth century. One of the Florentine dyers having ascertained, in the Levant, a method of extracting a colouring matter from the lichens which furnish archil, introduced this material into Florence on his return; by its sale he acquired an immense fortune, and became one of the principal men of the city.

The discovery of America tended greatly to the advancement of the art, as the dyers became supplied from thence with several valuable colouring materials previously unknown in the old world; amongst which are logwood, quercitron, Brazil-wood, cochineal, and annatto. A great improvement in dying also took place about the year 1560, which consisted in the introduction of a salt of tin as an occasional substitute for alum. With cochineal, the salt of tin was found to afford a colour far surpassing in brilliancy any of the ancient dyes. The merit of this application is attributed to Cornelius Drebbel, a Dutch chemist, whose son-in-law established an extensive dye-house at Bow, near London, about the year 1563.

About the middle of the sixteenth century, logwood and indigo began to be employed in Europe as dyes, but not without considerable opposition from the cultivators of the native woad. The use of logwood was prohibited, in England, by Queen Elizabeth, by a very heavy penalty, and all found in the country was ordered to be destroyed. Its use was not permitted in England till the reign of Charles the Second. Indigo, one of the most valuable and important of dye-stuffs, was also forbidden to be used in England and on the Continent, and denounced as "food for the devil."

These, and similar prejudices, were gradually surmounted, and in the eighteenth century the art of dyeing made very considerable progress. Madder, from which the colour known as Turkey or Adrianople red is produced, then began to be properly appreciated; and quercitron, a fine yellow dye, was brought extensively into notice by Dr. Bancroft. But the chief improvements of the moderns in this art consist in the employment of pure mordants, and in the application of colours derived from mineral compounds, as peroxide of iron, Prussian-blue, chrome-yellow, chrome-orange, manganese-brown, &c. Each of these colouring matters may be obtained as an insoluble precipitate on mixing together two solutions: in the dyeing processes the proper solutions are made to mix and produce the precipitate within the fibre, by impregnating it first with one solution, and afterwards with the other. As the precipitate thus produced is imprisoned within the fibre, it is not removable by mere washing with water.

The mode of dyeing Turkey red, which is the most durable vegetable colour known, was discovered in India. It was afterwards practised in other parts of Asia and in Greece; and, about the middle of last century, dye-works for this colour were established near Rouen and in Languedoc by some Greek dyers- In 1765, the French government, convinced of the im.

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portance of the process, caused an account of it to be published; but it was not introduced into this country until the end of last century, when a Turkey-red dye-house was established in Manchester by M. Borelle, a Frenchman. M. Borelle obtained a grant from Government for the disclosure of his process, but the method, which was published, does not seem to have been very successful. A better process was introduced into Glasgow about the same time by another Frenchman, named Papillon. Previous to this, however, Mr. Wilson of Ainsworth, near Manchester, had obtained the secret from the Greeks of Smyrna, and published it in two essays, read before the Literary and Philosophical Society of Manchester; but the process was said to be expensive, tedious, and less applicable to manufactured goods than to cotton in the skein. The greater part of the Turkey-red dyeing executed in this country is still carried on in the Glasgow district.

The ancients seem to have attained considerable proficiency in the art of topical dyeing, or of producing coloured patterns on cloths. The variegated linen cloths of Sidon are noticed by Homer, who lived nine hundred years before Christ, as very magnificent productions. In India the art of imparting a coloured pattern to a cotton fabric has been practised with great success from time immemorial, and it derives its English name of calico-printing from Calicut, a town in the province of Malabar, where it was formerly practised on a very considerable scale. According to Herodotus, who wrote more than four hundred years before Christ, the inhabitants of Caucasus adorned their garments with representations of various animals by means of an aqueous infusion of the leaves of a tree; and the colours thus obtained were said to be so fast as to be incapable of being removed by washing, and as durable as the cloth itself. The material of which the cloths were made is not stated, but they were probably woollen, as that part of Asia was then, as at present, celebrated for the superior quality of its wool.

From the following account by Pliny of the nature of the process of topical dyeing practised by the ancient Egyptians, it would appear that this people had attained such proficiency in the art, as could only have been originally acquired by extensive practice and close observation.

"An extraordinary method of staining cloths is practised in Egypt. They there take white cloths, and apply to them, not colours, but certain drugs which have the power of absorbing or drinking in colour; and in the cloths so operated on there is not the smallest appearance of any dye or tincture. These cloths are then put in a cauldron of some colouring matter, scalding hot, and after having remained a time are withdrawn, all stained and painted in various colours. This is indeed a wonderful process, seeing that there is, in the said cauldron, only one kind of colouring material; yet from it the cloth acquires this and that colour, and the boiling liquor itself also changes, according to the quality and nature of the dye-absorbing drugs which were at first laid on the white cloth. And these stains or colours, moreover, are so firmly fixed as to be incapable of being removed by washing. If the scalding liquor were composed of various tinctures and colours, it would doubtless have confounded them all in one on the cloth; but here one liquor gives a variety of colours, according to the drugs previously applied. The colours of the cloths thus prepared are always more firm and durable than if the cloths were not dipped into the boiling cauldron." (Pliny, Hist. Nat., lib. xxxv. cap. 11.) In as few words the principle of the common operations of calico-printing could hardly be more accurately described.

The *pallampoors*, or large cotton chintz counterpanes, made in the East Indies from a very early period, have similar dye-absorbing drugs applied to them by the pencil, and certain parts of the cloth are coated with wax to prevent the absorption of colour when immersed into the vessel containing the dye.

The topical dyeing of cotton goods seems to have been practised for a considerable time in Mexico. When Cortez conquered that country, he sent to Charles V. cotton garments with black, red, yellow, green, and blue figures. The North American Indians have also been for a long time in possession of a mode of applying patterns in different colours to cloth.

The art of calico-printing does not appear to have been much practised in Europe until the close of the seventeenth or the beginning of the eighteenth century, when Augsburg became famous for its printed cottons and linens. From that city the manufactures of Alsace and Switzerland were long supplied with colour-mixers, dyers, &c. The first print-ground in England was founded by a Frenchman on the banks of the Thames near Richmond, and soon afterwards a more considerable one was established at Bromley Hall in Essex. Several others were some time afterwards founded in Surrey, in order to supply the London shops with chintzes, the importation of which from India had been prohibited by an act of parliament passed in 1700, on account of the excessive clamours of the silk and woollen weavers. Though merely intended as a protection to the English silk and woollen manufacturers, this act had the effect of greatly stimulating and increasing the infant art of calico-printing; for the demand for printed calicos and chintzes could then be gratified only by printing, in this country, white Indian calicos, the importation of which was still allowed under a duty. An excise duty of threepence per square yard was imposed on the printed calicos in 1712, which was increased to sixpence in 1714; but the importation of calico being still considerable, a new alarm was raised, and a law enacted in 1720, which prohibited the wearing of all printed calicos whatever, whether of foreign or home production. The operations of the printer were then confined to the printing of linens.

The oppressive and absurd act of 1720 was repealed in 1730; but the calicos then permitted to be printed were to have the warp of linen and merely the heft of cotton, and were subject to a duty of sixpence per square yard. With such discouragements, the progress made in calico-printing was extremely slow: so lately as the middle of last century it was computed that only fifty thousand pieces of the mixed cloth were printed annually in the whole of Great Britain; whereas, at the present time, several manufacturers turn out as much as three and four hundred thousand pieces per annum each. The part of the act of 1730 by which the warp was required to be made of linen yarn was repealed in 1774; but the printed calicos were still subject to a duty of threepence-halfpenny per square yard, the repeal of which, in 1831, has been of the utmost advantage both to the manufacturer and the consumer.

The wonderful developement which calico-printing has received within the last half-century is to be attributed, in a great measure, to the adaptation of numerous ingenious mechanical inventions. The improvement in patterns, and the reduction in the price of cotton prints during this period, are striking illustrations of the advancement which has been made in machinery. The first improvement on the original wooden hand-printing block,* which is quite similar to the block of a wood-engraving, consisted in the substitution, for some styles of work, of copper plates, about three feet square (similar to those employed for printing engravings on paper), on which a much more delicate pattern could be engraved than on wood. The colour being laid on the copper plate, and the superfluous colour removed by a thin steel scraper, the plate was passed with the

* A description of the various modes of printing cloths now practised will be found in another part of the present article.

cloth through a press similar in principle to that of a copper-plate printer. The engraving of the plate was executed either by a common graver or by a punch.

The greatest mechanical improvement ever effected in this art was the invention of cylinder or roller printing, which is said to have been first made by a calico-printer at Jouy in France, named Oberkampf, in whose hands alone it remained for some time. The invention appears also to have been made independently by a Scotchman of the name of Bell, and was first successfully applied in the large way about the year 1785, at Monsey near Preston. Cylinder printing has received its greatest developement in Lancashire; and the perfection to which the process has been there brought is the chief cause of the admitted superiority of our calico-printing establishments over those on the Continent, where cylinder printing is comparatively but little practised.

Printing by the cylinder is executed with not only greater accuracy than by the wooden block, but with a saving of time and labour almost incredible. One cylinder machine, attended by one man to regulate the rollers, is capable of printing as many pieces as a hundred men and a hundred girls could with the hand-block during the same time; or as much work may be executed by a cylinder machine in four minutes as by the ordinary method of block-printing in six hours. A length of calico equal to one mile has been printed off with four different colours in a single hour.

The successful application of an engraved copper cylinder was followed by that of a wooden roller having the pattern in relief, the mode of printing by which is known as "surface printing." The "union" or "mule machine," which is a combination in one machine of the engraved copper cylinder with the wooden roller in relief, was invented about 1805 by Mr. James Burton of Church, near Blackburn.

One of the most important of recent improvements in the mechanical department of calico-printing is, a very ingenious method of executing block-printing with several colours by press-work in an arrangement similar to one of the modern type-printing machines. (An account of this mode of printing is contained in another section of the present paper.) Another important modern improvement, more particularly adapted to the press-machine, consists in the substitution of stereotype blocks made of a mixed metal, tin, lead, and bismuth, in the place of the wooden block.

During the last century the chemical principles of dyeing and calico-printing were investigated by Dufay, Hellot, Bergmann, Macquer, and Berthollet, and numerous and valuable improvements were suggested by some of their researches. The application of chlorine, by Berthollet, to the bleaching of tissues, especially cotton and flax, contributed in no small degree to the advancement of these arts; it is during the present century, however, and from the researches of numerous chemists still living, that they have received the most essential assistance from chemistry. The chief improvements introduced by the moderns consist, as already observed, in the application of colours derived from mineral substances.

Among the earliest introduced of this class of bodies, were iron buff and Scheele's green, which were followed by antimony orange (first applied by Mr. Mercer) and Prussian blue. The two chromates of lead (chrome-yellow and chrome-orange) were next introduced by M. Kœchlin of Mulhausen in 1821, and a few years afterwards Mr. Mercer first applied, on the large scale, the peroxide of manganese, known as manganese bronze.

§ II. GENERAL PROPERTIES OF VEGETABLE COLOURING MATTERS.

By far the greater number of the colouring matters employed in the art of dyeing are derived from vegetables, but the animal and mineral kingdoms also contribute a small number. Colouring principles are abundantly distributed over all the organs of vegetables, but never in a state of purity; they are always mixed, more or less, with other substances, and their isolation in a pure state often requires very complicated processes. Only a small number, comparatively, of these substances have as yet been obtained sufficiently pure to have their chemical composition determined. Like almost all other vegetable principles, they are composed either of carbon, hydrogen, and oxygen, or else of the preceding elements together with nitrogen, and have received particular designations derived in general from the names of the plants by which they are furnished. The most common colour of the vegetable kingdom is green, but as the substance which gives rise to this colour in leaves and trees is of an unctuous nature, it cannot be easily applied to cloth: to obtain a green, the dyer generally has recourse to the admixture of a yellow with a blue colouring matter. It is remarkable that the most vivid and brilliant of vegetable colours, namely, those of flowers and other parts of the plant exposed to solar light, are so small in quantity, and so fugitive, that they are of all the most difficult to isolate. In the organs which are protected from the light, as the interior of stems, branches, and roots, the colouring matters are generally devoid of all brilliancy, but when separated from the accompanying substances, they exhibit considerable lustre, and are by far the most durable.

Nearly all the colouring matters of plants which are capable of being isolated are yellow, brown, and red; the only blue substances which have been procured from plants are indigo and litmus, and no black vegetable substance, strictly speaking, has ever been isolated.

As a particular class of bodies, vegetable colouring matters do not possess many chemical characters in common; they are associated rather on account of their common application in the arts, than from the possession of similar properties. Most of them are entitled to be ranked among acids, but others are strictly neutral. By far the greater number of them are soluble in water, and always in larger proportion in hot than cold water. Those which are insoluble in water generally dissolve in alcohol, ether, and fixed oils.

In dry air, vegetable colouring matters appear to be permanent, but in humid air, and especially under the influence of the solar rays, they gradually lose colour, and become converted, by the absorption of oxygen from the air, into yellowish brown or colourless compounds. The ultimate action of air or oxygen on organic colouring matters in the presence of moisture, is to convert their carbon into carbonic acid, and their hydrogen into water. Solutions of organic colouring matters in water are acted on by oxygen with far greater facility than the dry colours.

The colour of some of these bodies is changed in a very remarkable manner by the application of acids and alkalies. The blue colour of most flowers, that of the flowers of the violet, for instance, is rendered red by acids, and green by alkalies. The purple infusion obtained by boiling red cabbage in water is affected in a similar manner; acids produce with it a lively red, and alkalies a full green. If the dried petals of the red rose are digested in spirits of wine, or hot water, they lose their colour without affording any, or at most only a trace of colour to the liquid. On adding a few drops of sulphuric acid, however, the liquid immediately acquires a fine red colour, and, if a slight excess of an alkali is afterwards added, it becomes green. The change from red to green may be produced indefinitely. The purple colour of litmus is rendered red by an acid, and blue, not green, by an alkali.

Some animal and vegetable colouring matters must undoubtedly be regarded as neutral bodies, that is, as possessing neither the characters of an acid nor those of a base; but most of them, particularly such as are soluble in water, have all the essential characters of a weak acid, being capable of uniting with and neutralizing salifiable bases, as potash, soda, lime, magnesia, alumina, &c. This tendency to combination is not confined, as some have supposed, to soluble colouring matters and insoluble bases; but the union is more obvious in such cases, as the resulting compound is always insoluble, while soluble bases usually form soluble compounds with soluble colouring matters.

For alumina and certain metallic peroxides, especially peroxide of iron and peroxide of tin, some organic colouring matters possess an energetic attraction. The pigments commonly called *lakes* are insoluble compounds of colouring matters with alumina or oxide of tin, which may be formed by mixing a solution of alum or of perchloride of tin* with the infusion of the dye-stuff, and adding afterwards an alkaline carbonate to liberate peroxide of tin or alumina: as the latter precipitates, it unites with and carries down the colouring matter in solution, frequently leaving the supernatant liquid entirely colourless. The infusion of the dye-stuff is sometimes made with an alkaline liquor, and mixed with a solution of alum after being filtered. In this way *yellow lake* is made with a decoction of turmeric, and annatto and quercitron lakes from the respective dye-stuffs.

Important applications are made in dyeing and calico-printing of the attraction which exists between alumina and metallic peroxides on the one hand, and

* Commonly called spirits of tin.

organic colouring principles on the other. By first impregnating a piece of cloth with alumina, green oxide of chromium, peroxide of iron, or peroxide of tin, and then dipping it into the infusion of the dye-stuff, the colouring matter leaves the solution to unite with the base, forming an insoluble compound, whereby it becomes strongly attached to the tissue, and is rendered less susceptible of alteration by the air, the solar rays, and other decomposing agents.

The attractive force of colouring matters for insoluble bases has been regarded by some as a mere attraction of surface, analogous to, if not identical with, the force of cohesion or adhesion, being the same as the attractive power by which charcoal is enabled to withdraw colouring substances from their solutions, and also the same as that by which a solid body condenses a permanent gas upon its surface. This mechanical attraction, which always exerts itself between a solid on the one hand, and a substance in solution or a gas on the other, depends entirely on the state of the surface of the solid, and is in no way connected with the chemical relations of the combining substances.

But the combinations of alumina, &c. with soluble colouring matters seem to be cases of true chemical combination, taking place in definite proportions, and under the influence of different degrees of attractive force for different colouring principles. Thus, alumina has a stronger attraction for the colouring principle of madder than for that of logwood, and a stronger attraction for that of logwood than for that of quercitron. When a piece of cloth impregnated with alumina is immersed in a decoction of quercitron bark, it acquires a fast yellow colour; if the same cloth is washed for some time and kept in a hot decoction of logwood, the alumina parts with the colouring principle of quercitron to combine with that of logwood, and the colour of the cloth becomes changed from yellow to purple. If the same cloth is next immersed for a few hours in a hot infusion of madder, the alumina parts with the colouring principle of logwood to unite with that of madder, the colour of the cloth changing from purple to red. The quantity of alumina on the cloth does not appear to diminish while these substitutions are taking place. These interesting facts were communicated to me by Mr. John Thom of the Mayfield print-works.

By contact with chlorine, and in presence of a little moisture, the colour of most, but not all, vegetable and animal dye-stuffs is instantly destroyed; the organic substance is decomposed, being commonly converted into colourless products, from which the original colour cannot be reproduced by any known process. In at least one case, however, which is that of indigo, the colour is reproducible after having been discharged by chlorine, provided the quantity of chlorine applied to the indigo has been no more than sufficient to change the blue colour to a buff, and not enough to destroy all colour. The rich crimson colour into which some preparations of indigo are changed by chlorine is also convertible into blue, though not to so deep a shade as the original indigo (Mr. Mercer).

In most cases of the destruction of vegetable colours by chlorine, the decomposition is effected, without doubt, through the powerful affinity of chlorine for hydrogen, which may be manifested in two ways; 1st, in the direct abstraction of hydrogen from the organic substance, and, 2ndly, in the decomposition of water, the hydrogen of which unites with the chlorine to form hydrochloric acid, while the oxygen of the water decomposes the colouring matter, forming carbonic acid with its carbon, and water with its hydrogen. Chlorine does not bleach readily in the absence of all moisture, and hydrochloric and carbonic acids may generally be discovered among the products. In a few cases, however, the bleaching action of chlorine simply consists in the direct combination of the chlorine with the colouring matter to form a compound which is devoid of colour.

Chromic acid is another powerful bleaching agent, which acts by affording oxygen to the colouring matter, becoming itself reduced to the state of green oxide of chromium. The colour of the vegetable substance is even more readily destroyed than if chlorine had been applied.

Most vegetable colouring matters are also bleached by sulphurous acid in the presence of water. The action of this substance is not so energetic as that of chlorine, and differs from it essentially in the circumstance that the colours are not entirely destroyed, but may in general be restored by exposure to the air, or by the application of a stronger acid or an alkali.

It is uncertain whether the bleaching power of sulphurous acid depends on the partial deoxidation of the colouring matter, or on the union of the sulphurous acid with the colouring matter to form a colourless combination.

Charcoal has also been classed among bleaching agents, as it readily withdraws colouring matters from their solutions, frequently leaving the supernatant liquid entirely colourless. The charcoal which absorbs colouring matters with most avidity is that obtained by the calcination of bones and other animal matters, the superiority of which seems to depend merely on its minute state of division, whereby the contact of the liquid and charcoal is rendered more perfect. The action of charcoal in bleaching vegetable infusions is altogether different from that of chlorine, and also from that of sulphurous acid. The colouring matter is not decomposed, but is merely mechanically attached to the surface of the charcoal, without having experienced any chemical alteration whatever.

When brought into contact with deoxidizing agents, several organic colouring matters part with a portion of their oxygen, and at the same time lose their colour. But if afterwards exposed to the air, or any source of free oxygen, the deoxidized bodies reassume oxygen, and with that element their original colour. The coloured bodies would therefore appear to be compounds of oxygen with a colourless radical. The alternate reduction and oxidation may be practised on the same substance indefinitely. As examples of colouring matters susceptible of these changes, may be mentioned litmus, logwood, Brazilwood, sapanwood, peachwood, red beet-root, and the red-cabbage. The most convenient deoxidizing agents to be employed in such experiments are the following:

1°. A mixture of granulated or feathered tin and a caustic alkali.

2°. Protoxide of iron, or protoxide of tin, recently precipitated, and still moist.

3°. Hydrogen gas, applied in the nascent state, by introducing a piece of zinc or iron into the infusion of the colouring matter, rendered acid by the addition of muriatic or sulphuric acid.

4°. Sulphuretted hydrogen gas, a stream of which may be passed through the coloured infusion, or the latter may be agitated in a jar containing the gas. As the colour disappears, a whitish precipitate of sulphur is produced.

5°. Double metallic sulphur salts containing an alkaline sulphuret, such as the sulphuret of arsenic and potassium (sulpharsenite of potash).

It is worthy of note that the colourless or white radicals of Brazil-wood, logwood, sapanwood, &c. do not unite with alumina and metallic peroxides to form insoluble compounds or lakes, like their oxides, or the true colouring matters.

Other vegetable colouring principles than those above mentioned become converted into colourless substances when exposed to the action of deoxidizing agents, but the chemical change which some of them suffer appears to be the acquisition of hydrogen instead of the yielding up of oxygen. When exposed to the air or other source of free oxygen, this hydrogen is removed, and the original colour returns. Indigo is one of the colouring matters susceptible of such changes.

Several colouring principles are contained in the plants from which they are derived in their white, deoxidized, or hydruretted state. Such is the case, for example, with indigo. That substance does not exist in the blue or dehydruretted state in the plant by which it is furnished, but as white indigo, or indigotin, the colourless hydruret of indigo blue. Most vegetable juices, the recent pulp of fruits, detached leaves, &c. become coloured brown and yellow by exposure to the air, from the absorption of oxygen. If carefully kept in a vessel of some gas devoid of free oxygen, such bodies experience no change in colour.

Colouring matters have the property of uniting with animal and vegetable tissues, by virtue of an attraction of surface quite similar to that by which they unite to animal charcoal. When well-scoured wool or silk is digested in a decoction of cochineal, logwood, or Brazil wood, or a solution of sulphate of indigo, it abstracts the colour so completely as to leave the liquid colourless, as if animal charcoal had been introduced. The affinity of vegetable tissues for colouring matters is in general not so great as that of animal tissues for the same substances. The vegetable fibre readily combines with a colouring material; but unless the latter is insoluble in water, the combination is exceedingly feeble. A familiar example of the affinity of the vegetable fibre for organic colouring matters is presented in the staining of a linen napkin by red wine. The portion of the cloth on which the wine falls soon abstracts the whole colour from the liquid, becoming dyed red; but beyond the spot thus produced, the cloth becomes moist without acquiring an appreciable colour, the wine having been deprived of all its colour by the portion of the cloth with which it came first into contact. The attractive force by which this result is obtained must not be considered as peculiarly subsisting between tissues and organic colouring matters, as many mineral substances are withdrawn from their solutions by tissues in quite a similar manner. Thus, cotton cloth readily separates lime from lime-water,* and the insoluble sulphate of alumina from an aqueous solution of basic alum.

Vegetable and animal colouring principles are divisible into two classes, with reference to their solubility or insolubility in water. Those which are soluble readily attach themselves to tissues, but only with a feeble affinity, as they may be separated by continued washing in water, especially with the assistance of heat. Logwood, madder, Brazil-wood, cochineal, and, in fact, the greater number of dyestuffs, belong to this class. To unite them firmly to a tissue, another substance is applied, which possesses the property of forming an insoluble combination with the colouring matter. Those colouring matters which are of themselves insoluble, or but slightly soluble in water, generally form, as might be expected, much faster combinations with tissues. Indigo, annotta, safflower, and such yellow and brown dyes as contain tannin combined with substances of the nature of apothème, are the principal members

* The separation of lime from lime-water by cotton cloth is exhibited when a drop of a solution of bleaching powder (which always contains free lime) is allowed to fall on a piece of cotton dyed with indigo. On the spot where the solution first touches the cloth, the colour remains unaltered, the lime only having been there intimately absorbed; but on the ring surrounding this spot, the colour becomes discharged through the action of the chloride of lime.

of this class. To effect their solution, some other solvent than pure water must be applied. Thus, indigo is dissolved by bringing it, through the action of a deoxidizing agent, to the state of white indigo or indigotin, which is soluble in water in the presence of an alkali or some lime. If a piece of cloth is dipped into such a solution, the white indigo is absorbed into the pores of the fibres, and on exposing the cloth to the air, imbibes oxygen, by which it becomes converted into the original insoluble indigo blue. The latter remains firmly attached to the fibre, being imprisoned within the pores, and therefore incapable of being removed by mere washing in water. The colouring matters of annotta and safflower, though very sparingly soluble in water, are easily dissolved by alkaline liquids, from which they may be precipitated on the addition of an acid. A piece of silk might be dyed with either of these colours, by first impregnating it with the alkaline infusion of the dye-stuff, and then passing it through a weak acid: the best method, however, of dyeing both silk and cotton with annatto or safflower is by wincing the piece in an imperfectly neutralized alkaline infusion of the dye-stuff, which contains the colouring matter in a state of feeble suspension, readily precipitated on a solid body presenting a finely divided surface, such as cloth. The partial neutralization of the alkali in this process is effected by a very weak acid or an acidulous salt, such as bitartrate of potash (cream of tartar).

Such are the principal general properties of organic colouring principles, a knowledge of which is of the highest importance to the practical dyer and calico-printer. But these bodies differ so much from each other in many respects, that the best means of extracting them from the organs by which they are produced, and the most effectual manner of applying them to textile fabrics, can only be discovered by the accurate investigation of the chemical and general properties of each distinct colouring matter separately.

Nature of colour.—The appearance of colour may almost be regarded as an optical delusion, since it does not exist in the object, but in the light which the object reflects. It is well known that a ray of white light from the sun is resolvable into three rays of the primary colours, red, yellow, and blue. As a mixture or combination of these three coloured rays, white or colourless light may be considered, the absence of colour depending on the exact equilibrium of the three. When the coloured rays are partially separated by the refractive force of a glass prism, an image or spectrum is obtained, presenting seven different colours, namely, red, orange, yellow, green, blue, indigo, and violet. The orange, green, indigo, and violet tints proceed from the intermixture in various proportions of the three primary rays.

Among opaque substances, there are some which completely absorb the three coloured rays incident on their surface, and therefore, having no light to reflect to the eye, appear *black*. Others, on the contrary, reflect all the light, and are consequently *white*. But others possess the power of decomposing the light, that is, of absorbing the whole or a portion of one of the three primary rays and reflecting the remainder; or, it may be, of absorbing unequal proportions of each of the three rays. When such is the case, the body appears to be coloured, not from the inherent possession of a colour, but because the light which it reflects to the eye is not homogeneous white light. A blue substance, for example, is said to reflect the blue rays only, or in greatest proportion, the yellow and red rays being absorbed. If red, it is said to absorb the yellow and blue rays, and reflect the red; and by the absorption of the rays in unequal proportions, and by the reflection of more or less of the white or undecomposed light, every shade of colour may be produced. The same remarks apply to transparent coloured substances; only, instead of the decomposed light being reflected to the eye, it is transmitted. According to this manner of viewing the colouring principle, it has been observed that the art of dyeing consists in fixing upon stuffs, by means of molecular attraction, substances which act upon light in a manner different from the stuffs themselves.

The production of white by the combination of the three primary colours is practised in one of the finishing operations to which goods are subjected in the process of bleaching. To whatever length the ordinary operations may be continued, some kinds of goods always retain a brownish-yellow hue, which may be removed, and a pure white imparted, by applying a little smalts, indigo, archil, or a mixture of Prussian-blue and cochineal pink. In such cases the blue, or mixture of blue and pink, supplies the tints necessary to the production of white with the brownish-yellow colour of the goods. But when the dyer attempts to form white by combining red, yellow, and blue, he often obtains a dark brown, or black, because the resulting combination does not reflect as much light as the three coloured ingredients separately.

The following alphabetical list of colouring matters, with their origin, uses, and principal chemical characters, may prove useful for reference. The history and applications of some of them will be fully discussed in separate articles.

I. LIST OF VEGETABLE AND ANIMAL COLOURING MATTERS.

Alkanet. — The root of the *Anchusa tinctoria.* Its colouring principle, which is red, is nearly insoluble in water, but soluble in alcohol, ether, oil of turpentine, and fixed oils. It is used as a colouring matter for ointments and other unctuous preparations, but not in dyeing.

A variety of alkanet was formerly met with in commerce, derived from the roots of the *Lawsonia inermis.*

Annotta.—A hard paste prepared by inspissating the washings from the fermented seeds of the *Bixa orellana.* Its colouring matter is yellowish-red, nearly insoluble in water, soluble in alcohol and alkaline liquids. It forms an orange-coloured compound with alumina, a citron-yellow compound with protoxide of tin, and a greenish-yellow compound with protoxide of copper. It is used to dye silks golden-yellow, by simply digesting the goods in an alkaline solution of annotta, and orange-red by exposing them afterwards to the action of a dilute acid. It is also used to dye cotton yellow, with the aluminate of potash as the mordant, and as a colouring matter for cheese.

Archil.—A violet-coloured paste, made from different species of lichens: that of the Canaries, which is the most esteemed, is from the *lichen rocellus;* and that of Auvergne, from the *lichen parellus. Litmus*, *turnsole*, and *cudbear* are merely modifications of archil. The colouring principle of these dye-stuffs is soluble in water and alcohol, and its colour is changed by the weakest acids from purple or violet to bright red. It is a brilliant colour, but possesses little permanence, and is chiefly used to give a violet or purple bloom as a finish to silks and woollen cloths already dyed with other colours. It is rarely used for cotton goods.

Barwood.—This is a dull red dye-stuff, the colouring matter of which is only slightly soluble in water, but sufficiently so for dyeing without the application of another solvent, such as an alkaline liquid, in which it dissolves with facility. It gives red compounds with alumina and peroxide of tin, and is mostly used for dyeing silks and woollen cloth. The colouring matter of *camwood* is quite similar in its properties to that of barwood, but is somewhat brighter in colour. Both barwood and camwood possess much more permanence than peachwood, for which they are now frequently used as substitutes.

Brazil-wood. — This and *Sapanwood, Fernambouc-wood, Peachwood,* and *Nicaragua-wood,* are derived from certain species of Cesalpina. Their colouring matter, which seems to be identical, is red, soluble in water, rendered purple or blue by alkalies, and yellow by acids. It forms a red compound with alumina, a black compound with peroxide of iron, a violet compound with protoxide of tin, and a rose-coloured compound with peroxide of tin. It is of itself a fugitive colour, being easily bleached by light with exposure to the air; but its stability is considerably increased by being combined with peroxide of tin or alumina. It is used in dyeing wool, silk, and cotton with the tin and aluminous mordants. Of these woods peachwood and sapanwood are the most extensively employed at present.

Camwood.—(See Barwood.)

Catechu, or *terra Japonica.*—This is an extract from the heart-wood of the khair-tree of Bombay and Bengal (*mimosa catechu*), made by evaporating the decoction of the wood nearly to dryness. Its chief constituent is a variety of tannin, differing slightly in its characters from that contained in galls. Catechu is very soluble in water and alcohol, with the exception of a little earthy matter. It gives a rich brown-grey colour with nitrate of iron, a fast bronze by being oxidized through the agency of a mixture of sulphate or nitrate of copper and muriate of ammonia, a brownish-yellow with protochloride of tin, and a reddish-brown with acetate of alumina. It is extensively used in calico-printing as a topical brown, when mixed with nitrate, sulphate, or acetate of copper, and sal-ammoniac.

Cochineal.—A female insect found on the *cactus opuntia* or *nopal,* dried. Its colouring principle, termed *coccinellin,* is naturally of a purplish-red colour; it is soluble in water and weak alcohol; its colour is changed to red by acids, and to crimson by alkalies. It forms a fine crimson compound with alumina, a violet compound with protoxide of tin, and a scarlet compound with peroxide of tin. Wool and silk are dyed of a fine scarlet by means of a mixture of decoction of cochineal with cream of tartar and dyers' spirit, which is a mixture of protochloride and perchloride of tin; and of a crimson, by a decoction of cochineal with alum and perchloride of tin. Cochineal is also used in the preparation of the pigment called carmine.

Cudbear.—(See Archil.)

French berries, called also *Avignon berries* and *Persian berries*. The fruit of the *rhamnus infectorius*. The berries afford a bright yellow liquid when boiled in water, which gives a golden-yellow colour with protochloride of tin, a lemon-yellow with peroxide of tin, a rich yellow with alumina, and a drab with a salt of iron. They are much used as a bright yellow topical colour when combined with a tin or aluminous mordant.

Fustet or *yellow fustic.*—The wood of the *rhus cotinus*, the colouring matter of which is yellow. Being a fugitive dye-stuff, it is very little employed at present in dyeing processes.

Fustic or *old fustic.*—The wood of the *morus tinctoria*. Its aqueous decoction is orange-coloured, and is brightened by cream of tartar, alum, and solution of tin. Its principal use is to dye woollen and cotton cloths of a permanent yellow with an aluminous mordant. It is also used to produce a brownish tint with copperas.

Indigo.—A blue insoluble pigment procured by the oxidation of a colourless substance (indigotin) contained in the leaves of the *indigofera*, by subjecting the leaves to a process of fermentation. Indigo blue may be reconverted to indigotin by applying a deoxidizing agent, and then becomes soluble in alkaline liquids, in which form it may be applied to cloth (see page 244).

Kermes grains.—Dried female insects of the species *coccus ilicis*, which are found on the leaves of the *quercus ilex* or prickly oak. The decoction of kermes in water is red, and is rendered brownish by acids, and violet by alkalies. Kermes was formerly much used as a crimson dye with a mordant of alum, but it is now superseded by cochineal and lac-dye.

Lac-dye.—*Stick-lac* is an exudation produced by the puncture of an insect on the branches of several plants, by which the twig becomes incrusted with a brownish red resin. This is a complicated mixture, containing a small portion of a red colouring matter quite similar to that of cochineal. *Lac-dye* is the residue of the evaporation of the aqueous infusion of ground stick-lac. It is employed to dye wool of a brilliant scarlet colour with a mordant of dyers' spirit. The solution of the lac for this purpose is effected in very dilute muriatic acid.

Litmus.—(See Archil.)

Logwood.—(Campeachy wood.)—The wood of the *hæmatoxylon campechianum.* Though the colouring principle of logwood is red in its natural state, yet it forms blue or violet compounds with almost all metallic oxides. It is soluble in water, affording a reddish liquid, which is rendered purple by alkalies, or, if added in excess, brownish-yellow. It is employed in dyeing all kinds of stuffs of a variety of shades between light purple and black with an aluminous mordant, and between lilac and black with the acetate of iron as the mordant.

Madder.—Dutch madder is the root of the *rubia tinctorum*, and Turkey and French madder that of the *rubia peregrina.* According to M. Runge, madder contains five distinct colouring principles; madder red (called also *alizarine*), madder purple, madder orange, madder yellow, and madder brown. Madder red is soluble in water, but only in small proportion, and therefore cannot be employed in a concentrated solution. It is very extensively used in the dyeing and printing of cotton goods for the production of a permanent bright red colour with an aluminous mordant; of a lilac, purple, and black with oxide of iron; and of a variety of shades of chocolate with a mixture of the iron and aluminous mordants, with or without the addition of sumach. Turkey madder is preferred for producing the Turkey-red dye, pinks, and light lilacs; and Dutch madder for producing purples, chocolate, and black. A form of madder containing more colouring matter than the natural root is now met with in commerce, under the name of *garancine.* This article is said to be prepared by digesting powdered madder in cold oil of vitriol, which destroys most of the constituents of the root, but leaves the red colouring matter unaltered.

Nicaragua-wood.—(See Brazil-wood.)

Peachwood.—(See Brazil-wood.)

Quercitron.—The bark of the *quercus nigra*, or yellow oak, which grows in North America. Its colouring principle, which is yellow, is very soluble in water. Quercitron is much used to impart a yellow colour to cotton with the intervention of an aluminous mordant, and to produce drabs with an iron mordant, and olives with a mixture of the iron and aluminous mordants. It is also much used, when mixed with a small quantity of madder, to produce an orange with a mordant of alumina.

Safflower.— The flowers of the *carthamus tinctorius.* Safflower contains two colouring matters; a yellow substance soluble in water, which is of no value in dyeing; and a fine red substance, insoluble in water, but soluble in an alkaline liquid. It is used to dye silk and cotton of a rose colour by wincing the piece in an imperfectly neutralized alkaline infusion of the dye-stuff.

Sandal-wood.—(Red Sanders wood.)—The wood of the *pterocarpus santalinus.* Its colouring matter is red, scarcely soluble in water, but soluble in alkaline lyes. The colour may be applied to tissues by dipping them alternately in an alkaline decoction of sandal-wood and in some acidulous liquid. It does not stand exposure to light well.

Sapanwood.—(See Brazil-wood.)

Sumach, galls, valonia, and *sawwort.*— These and some other astringent vegetable productions are used to impart to cloth a variety of shades from slate colour to black, with peroxide of iron as the mordant. These matters can hardly be classed among colouring matters, as their active ingredients, tannic and gallic acids, are white when pure. By uniting with peroxide of iron, however, these acids form blueishblack compounds, which are the basis of common writing-ink, and may be communicated to cloth by first boiling the piece in a decoction of the astringent material, and afterwards digesting it in a solution of copperas. An infusion of logwood is commonly added to the solution of copperas. Vegetable astringent principles are also used in some other dyeing processes, in which their action seems to partake of that of a mordant.

Turmeric.—The root of the *curcuma longa.* Its colouring principle, which is orange-yellow, is slightly soluble in water, and readily soluble in an alkaline solution, becoming dark brown. As a dye, it is applied only to silk.

Turnsole.—(See Archil.)

Weld.—The entire dried plant, *reseda luteola.* Its decoction in water is yellow. Silk, woollen, and cotton goods may be dyed of a permanent and bright yellow by a decoction of weld with alumina or peroxide of tin as the mordant. With the latter, weld affords to cloth the fastest vegetable yellow colour we possess.

Woad.—The colouring matter of this plant (*isatis tinctorea*) seems to be identical with indigo. Woad is commonly employed as a fermentative addition to indigo in the pastel vat.

II. LIST OF MINERAL COLOURS EMPLOYED IN DYEING.

Antimony orange.—This orange-red substance has been applied to cloth by passing the piece through a solution of the sulphuret of antimony and a little sulphur in a caustic alkali, and afterwards exposing it to the air to precipitate the sulphuret, through the absorption of carbonic acid.

Arseniate of chromium.—This is a fine grass-green coloured compound, which may be imparted to cloth, by the application, first of a solution of chloride of chromium, and afterwards of a solution of arseniate of soda.

Chrome-yellow, or *chromate of lead.*—The colour of this pigment is bright yellow; it may be communicated to cloth by the consecutive application of solutions of acetate or nitrate of lead and bichromate of potash; or the oxide of lead may be first fixed on the cloth in an insoluble state, as carbonate, tartrate, or sulphate. It consists of one equivalent of chromic acid and one equivalent of oxide of lead.

Chrome-orange, or *subchromate of lead.*—This is a dark orange-red pigment, consisting of one equivalent of chromic acid and two equivalents of oxide of lead. To apply it to cotton, the piece is first dyed with chrome-yellow, and is afterwards passed through hot milk of lime, by which a portion of the chromic acid of the chrome-yellow is separated.

Manganese brown (*hydrated peroxide of manganese.*)—Cloth is dyed with this substance by being passed, first, through a solution of sulphate or chloride of manganese; next, through a caustic alkaline solution, to precipitate protoxide of manganese; and lastly, through a solution of chloride of lime, to convert the protoxide of manganese into peroxide; or the peroxidation may be effected by mere exposure to air.

Orpiment (*sulpharsenious acid.*—This is a bright but alterable yellow, which may be communicated to silk, wool, and cotton, by first passing the goods through a solution of orpiment in ammonia, and afterwards suspending them in a warm atmosphere to volatilize the ammonia and precipitate the orpiment. This substance is sometimes applied in the form of a solution in a caustic fixed alkali, in which case the precipitation is afterwards effected by passing the cloth through dilute sulphuric acid.

Peroxide of iron (*iron buff*).—This oxide is applied to cloth to produce a yellowish-brown shade of different intensities, by passing the piece through a solution of a salt of the peroxide of iron, and a solution of an alkaline carbonate, in succession.

Prussiate of copper.—A delicate cinnamon colour is sometimes communicated to cotton by means of this substance, which is applied by first passing the cloth through a solution of sulphate of copper, then through a dilute alkali to precipitate oxide of copper, and lastly, wincing in a solution of yellow prussiate of potash, containing a little muriatic acid.

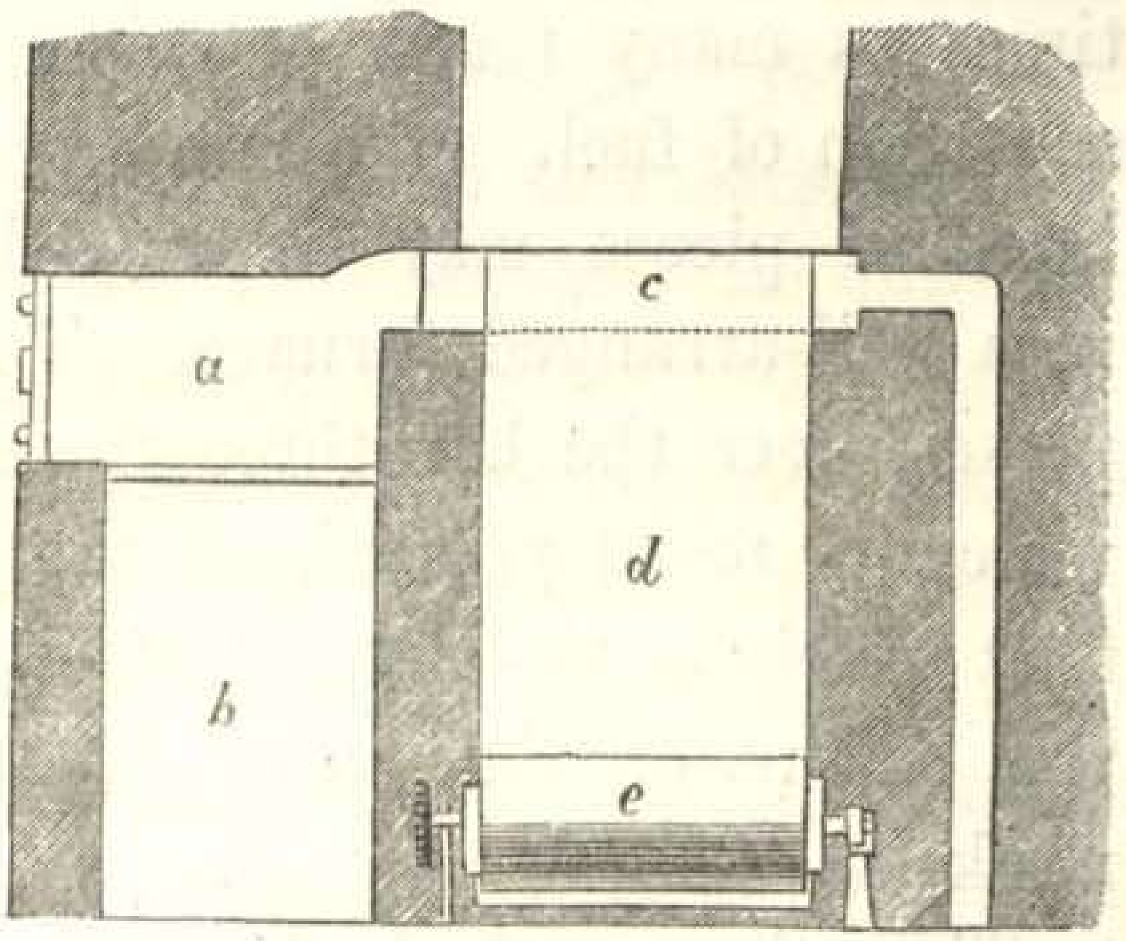
Prussian blue.—To apply this pigment, the cloth may be first impregnated with a solution of acetate of iron (iron liquor), and afterwards passed through a solution of yellow prussiate of potash, acidified with a little muriatic acid.

Scheele's green (*arsenite of copper*).—This grass-green coloured substance may be applied to cloth by the double decomposition of nitrate of copper and arsenite of potash; the cloth being passed through solutions of these salts consecutively. A better method is, first to precipitate oxide of copper on the cloth by the action of an alkali, and to wince the piece afterwards in a solution of arsenite of potash.

§ III. GENERAL NATURE OF DYEING PROCESSES.

The processes by which different kinds of textile fabrics are impregnated with the same colouring material are often very dissimilar, and few dyeing processes are applicable in their details to goods of cotton, silk, and wool. For this reason, the observations in the present section refer chiefly to cotton fabrics, the treatment of which requires greater assistance from chemistry than the more easily dyed animal tissues. The dyeing of cottons, however, is mostly practised as a part of the process of calico-printing; but the chemical principles involved in the different operations are precisely the same, whether the cloth is merely dyed and finished in that state, or both printed and dyed.*

Fig. 30.



The object of the first operation to which cotton goods are subjected, whether intended to be afterwards printed or merely dyed, is the removal of the fibrous down or nap on the surface of the cloth. This is effected by the process of *singeing*, which may be performed in two different ways equally efficacious.

* For detailed accounts of distinct dyeing processes, the reader is referred to other articles treating of individual colouring materials.

The old method consists in drawing the cloth swiftly over a red-hot semi-cylindrical bar of copper, three-quarters of an inch in thickness, placed horizontally over the flue of a fire-place, situated immediately at one end of the bar. The disposition of the different parts of a singeing furnace may be understood with the assistance of the sectional representation in fig. 30; *a* represents the fire-place, and *b* the ash-pit; *c* is the semi-cylindrical bar of copper, forming the top of the flue; and *d* is the strip of cotton, which is rapidly drawn over the ignited bar, and immediately passed round a wet roller, *e*, to cool from the effects of singeing. In the figure, the flue is represented as passing downwards to communicate with the common draught-chimney.

An iron bar, of two inches or more in thickness at the top, was formerly used instead of a copper bar; but the latter is found to last about ten times as long as the former, and to singe nearly three times as many pieces of cotton with the same consumption of fuel. With a copper bar, about fifteen hundred pieces may be singed by a ton of coals in a well-arranged furnace. The cotton is generally passed over the bar three times; twice on the side which is to be printed, or the "face," and once on that which is to be the "back." By this operation the colour of the calico becomes very similar to nankeen.

The other method of singeing consists in passing the cloth rapidly through a coal-gas flame, for which a patent was obtained by Mr. Hall of Basford, near Nottingham, in the year 1818. The gas issues from numerous perforations through the upper surface of a horizontal tube, and the cloth to be singed is drawn over the flame rapidly by rollers. In the method first patented, the flame is drawn up through the web of cotton or other fabric by a flue leading into a common draught-chimney; but the draught not being always sufficient to draw the flame through immediately, an improvement in the apparatus was devised by Mr. Hall, and patented in 1823, which consisted in placing immediately over the gas-flame a horizontal tube, with a slit lengthways through its lower surface, which tube is placed in communication with a fan or an exhausting apparatus. An arrangement of this kind, so constructed as to allow the passage of two pieces of cloth at the same time over two gas-flames, is capable of singeing, when properly managed, fifty pieces per hour.

That the colours of the tinctorial matters applied to tissues may appear in their purity, it is essential that the cloth be wholly freed from the foreign matters which adhere to its surface, whether imparted in the processes of spinning, weaving, &c., or else naturally adherent to the fibre of the cloth. In cotton goods, this is accomplished by the process of bleaching by means of chlorine; and in silk and woollen goods, by the action of sulphurous acid.

The ordinary operations practised in the process of bleaching by chlorine consist in subjecting the cloth to the successive action, 1°, of a dilute alkaline solution; 2°, of a dilute solution of chloride of lime or bleaching powder (commonly called "chemic" in bleach-works and print-works); and 3°, of dilute sulphuric acid. The operation of submitting the cloth to a solution of bleaching powder is known as "chemicking;" and to dilute sulphuric acid, as "souring." The action of sulphuric acid on the cloth impregnated with a solution of bleaching powder is to liberate chlorine by combining with the lime to form sulphate. The details of this important process will form the subject of another article; for the present, the following list of the successive operations to which a cotton fabric is subjected in order to prepare it for printing, will suffice for purposes of reference:

1. Washing in cold water,
2. Soaking for eight hours in boiling lime-water,
3. Washing in cold water,
4. Souring,
5. Washing,
6. Soaking for ten hours in a dilute solution of soda-ash,
7. Washing,
8. Chemicking,
9. Souring,
10. Washing,
11. Soaking in solution of soda-ash,
12. Washing,
13. Chemicking,
14. Souring,
15. Washing,
16. Soaking in hot water,
17. Squeezing and drying.

In the process of bleaching mousselin de laines by means of sulphurous acid, the goods are usually passed two or three times through a solution of soap and soda, at about the temperature 130° Fahr., and then exposed for several hours to the action of sulphurous acid gas, produced from burning sulphur in a close chamber. The latter operation is termed "sulphuring." The goods are next passed through a very weak solution of caustic soda, dried, and usually impregnated with a dilute solution of tin, which imparts considerable brilliancy to the colours afterwards applied to the goods. For this purpose, de laines (which are formed of cotton and wool) are impregnated with two different solutions of tin consecutively, one intended to afford oxide of tin to the wool, the other to the cotton. The solution first applied is a mixture of perchloride of tin and muriatic acid, for the wool; the others is stannate of potash;* from which oxide of tin is precipitated on the cotton by passing the piece afterwards through dilute sulphuric acid. For the finer work, the sulphuring of de laines is usually performed twice.

The only operations to which silken cloth is subjected preparatory to being printed, are, 1°, boiling in a solution of soap and soda to remove the "gum;" 2°, passing through dilute sulphuric acid; and 3°, washing and drying.

To impart a permanent dye to a tissue, it is essential that the colouring material, or the substances from which it is to be produced, should be applied in a state of *solution*, or in a condition to penetrate to the interior of the fibre of the cloth, either at its open extremity, or through the parietes. If a

* A solution of oxide of tin in caustic potash.

piece of cloth is dipped into common writing-ink, the black colour acquired by the cloth may be removed by washing with water, because the tannate of iron, which is the basis of the ink, instead of being in solution, is in an insoluble state, being merely suspended in the liquid, and therefore unable to enter the interior of the fibre. To apply the tannate of iron in a permanent manner, it is necessary to *produce it within the fibre*, which is accomplished by first imbuing the cloth with an infusion of galls or other liquid containing tannin, and afterwards with a solution of a salt of iron. That the colours in solution in the dye-beck should attach themselves to the stuff in the form of a compound insoluble in their original solvent, is the principle on which the dyeing of fast colours rests; and the more insoluble the compound in other liquids, so much the faster the colour.

In nearly all the different processes for dyeing cloths, the colour is applied by one of the four following methods:

1. From two solutions; the colouring material not existing in either separately, but produced on the mixture of the two. The cloth is first impregnated with one solution, and afterwards with the other.

2. From the solution of the colouring material; the cloth being first impregnated with some substance (usually existing on the cloth in the solid state), which has the property of combining with the colouring matter to form an insoluble compound.

3. From the solution of the colouring material

itself, or its basis; the cloth having previously undergone no essential preparation.

4. By effecting a chemical alteration of the fibre of the cloth, with the formation of a coloured product.

By the first method of dyeing, which is the simplest and most intelligible, all mineral colours, such as chrome-yellow, Prussian-blue, peroxide of iron (iron buff), and manganese-brown, may be applied to textile fabrics. The proper colouring matter in all these cases is insoluble in water, and is thrown down as a precipitate whenever the two solutions proper for its formation are mixed. Thus, whenever an aqueous solution of the salt called bichromate of potash is mixed with an aqueous solution of acetate of lead, an insoluble precipitate of chrome-yellow (chromate of lead) is produced. In like manner, Prussian-blue is precipitated when a solution of yellow prussiate of potash is mixed with a solution of a salt of the peroxide of iron. In the processes of dyeing cloth with these and all other mineral colours, the mixture of the proper solutions, and consequent formation of precipitate, is made to take place within the elongated cell or tube which forms the fibre of the cloth; so that the resulting solid, being imprisoned within the fibre, is rendered incapable of being removed by mechanical means. The fastness of colours applied to cloth in this way is entirely a mechanical effect, and in no way referable to a chemical attraction of the fibre for the colouring matter.

A piece of white cotton cloth moistened with either a solution of bichromate of potash or of acetate of lead, may be easily cleaned from every particle of the soluble bichromate or acetate by simply washing with water. But if the piece of cloth is first imbued with the solution of the acetate, and afterwards with the bichromate, (or the order of impregnation may be reversed,) the precipitate of chrome-yellow is produced within the fibre, and can never be removed by washing with water. The chrome-yellow that is washed away in this experiment was merely loosely attached to the exterior of the fibre. It may be observed here, that as all the colouring matter which is deposited on the exterior of the fibre is a loss of material, it is advantageous to remove the excess of the solution with which the cloth is first imbued, by draining, squeezing, and sometimes by slightly washing the cloth when taken out of the first solution and about to be immersed in the second.

So far as the mere operations are concerned, the processes now commonly practised for applying mineral colours to cloth, are rather referable to the second style of dyeing according to the classification here adopted. Instead of passing the cloth through the two solutions consecutively, one of the two materials, usually the base of the mineral colouring matter, is first applied in an insoluble state, and the cloth is afterwards winced or agitated in a *dilute* solution of the other. To apply ferro-prussiate of copper, for example, to cotton in this way, the piece is first impregnated with a solution of sulphate of copper. The oxide of copper is, in the next place, fixed in an insoluble state by passing the cloth through a dilute alkaline solution; and the prussiate of copper is formed, lastly, by wincing the cloth in a dilute solution of yellow prussiate of potash containing a little muriatic acid. The economization of the solution last applied is the chief advantage of such a mode of proceeding over the old method of applying the two solutions in succession, without the fixation of a substance derived from the first; since the production of any superfluous colouring material is entirely avoided. In the process of dyeing cotton with chrome-yellow, the same depth of colour may be imparted to a piece containing precipitated oxide or carbonate of lead, from a solution of eight ounces of bichromate of potash to a gallon of water, as from a solution of twenty-four ounces of bichromate in a gallon of water, when the cloth contains only the soluble acetate or nitrate. It is to be observed, that although the mere operations in this kind of work are the same as those of the second style to be noticed immediately, yet the principles of the two styles are dissimilar, for the colouring material is not contained in the second solution any more than in the first.

To apply to cloth in a permanent manner those colouring substances which are naturally soluble in water, and have not in themselves a strong affinity for tissues (see page 243), of which kind are the greater number of vegetable and animal tinctorial matters, it is essentially necessary to effect their conversion on the cloth into compounds which are insoluble in water. This is accomplished by first applying to the cloth some substance (most frequently the sub-salt of a metallic oxide) which has an affinity for the colouring matter, whereby it is enabled to withdraw it from the solution and convert it into an insoluble compound. The substance which thus acts as the bond of union between the tissue and the colouring matter, is distinguished as the *mordant.* One circumstance in which this style of dyeing differs from the preceding is, that in this, the mordant must be applied to the cloth before the colouring matter, except in some cases where both may be applied at the same time; but with mineral colours, which may be imparted by the successive application of two solutions, it is generally a matter of indifference which of the two solutions the cloth is first impregnated with.

In its common acceptation by the practical dyer the term mordant is as indefinite as it is inappropriate, since it includes any kind of substance which can facilitate the application of a dye-stuff to a tissue. Properly speaking, a mordant is a substance which has an attraction of surface for the tissue, a chemical affinity for the colouring matter in solution (see page 236), and the property of forming an insoluble compound with the colouring matter. By virtue of the combination of these properties, it is enabled to effect in a durable manner the union of the tissue with the colouring substance.

But with the practical dyer, the term mordant has a much wider signification; even the solvent of the dye-stuff, if the latter is insoluble in water, receives that designation; thus sulphuric acid is sometimes termed a mordant when employed as a solvent for indigo in the preparation of Saxon blue. The name, which was given by some French dyers at a time when little was known respecting the chemical principles of dyeing, is derived from *mordere*, to bite; the mordant being supposed to exert a corrosive action on the fibre which serves to expand the pores and allow the absorption of the colour.

In most cases of cotton dyeing with the intervention of a mordant, the latter must exist on the cloth about to be dyed in a form insoluble in water. But as it is also essential that the mordant should be contained in the interior of the fibre of the cloth, it must be applied at first in a state of solution, for no substance in a solid form can penetrate to the interior of the fibre. The cloth, therefore, must be first impregnated with a liquid, by the decomposition of which the insoluble substance is to be produced.

The form in which a mordant exists on a piece of cloth ready to be dyed is usually that of a sub-salt; that is, a body of a saline constitution (consisting of an acid and a base), in which the proportion of base is in considerable excess. When a piece of cotton, for example, is moistened with a solution of basic alum (soluble subsulphate of alumina) and dried, an insoluble subsulphate of alumina is produced on the cloth, containing less sulphuric acid than exists in the soluble subsulphate. It is not probable, however, that, when the cloth thus mordanted is immersed in the dye-beck, the insoluble sub-salt combines as such with the colouring matter in solution; the combination, which is doubtless a chemical one, takes place between the colouring matter and the base of the sub-salt. In this case, either all the acid of the sub-salt or else the corresponding soluble neutral salt is liberated and dissolved, the whole or the excess of base remaining on the cloth to fix the colouring material.

When a piece of cotton impregnated with subsulphate of alumina, for example, is put into the madder-beck, the colouring matter of the madder combines with either the whole of the alumina in the subsulphate, or else that portion of the alumina only which is in excess over the amount contained in the soluble sulphate. In the first case, the subsulphate of alumina is simply decomposed into alumina on the one hand, and sulphuric acid on the other; while in the second case it is resolved into alumina on one side, and the soluble and neutral sulphate on the other.

From the preceding observations may be inferred the necessity of distinguishing between the three states in which a mordant may exist; namely, first, in the soluble form in which it is applied to the cloth; second, as the insoluble sub-salt afterwards produced in the fibre; and third, as the true base existing in union with the colouring matter in the dyed cloth. The term mordant ought strictly to be confined to the true base in whatever form it exists; but for convenience, it is also applied to the first solution, and to the sub-salt on the cloth before the dyeing.

In a few cases, however, the insoluble substance which is precipitated on the cloth from the solution of the mordant is not a sub-salt, but the true mordant or base itself; thus, pure alumina may be precipitated from the solution of aluminate of potash, and pure peroxide of tin from the solution of stannate of potash.

If the affinity of the colouring matter for the mordant is so powerful that a compound of the two is precipitated immediately on their solutions being placed in contact, the intermediate step, consisting in the formation of the insoluble sub-salt by drying, is sometimes omitted. The cloth is then first impregnated with the solution of the mordant, and after being washed, drained, and squeezed, is passed through the solution of the colouring matter. It frequently happens, however, and especially with wool and silk, that even in these cases an insoluble sub-salt does attach itself to the fibre from the solution; but it is commonly produced on cotton during the desiccation of the mordanted goods.

In all cases where the formation of an insoluble sub-salt by the desiccation of the mordant on the cloth is omitted, the excess of mordant which remains on the surface of the cloth is removed by washing and draining, before the cloth is exposed to the dyeing liquid. This excess of mordant is removed for three reasons; 1°, to prevent an unnecessary abstraction of colouring matter from the dye-beck; 2°, to ensure a more uniform distribution of tint; and 3°, to attach the colour in a more permanent manner. When the solution of the mordant produces an immediate precipitate with that of the colouring matter, if the excess of mordant is allowed to remain on the cloth, the latter assumes a good colour when put into the dye-beck, but which is, for the most part, merely attached to the surface, very little existing in the interior of the fibre. This seems to arise from the closing of the apertures through which a liquid obtains access to the interior of the tube or cell, by the precipitate of colouring matter.

But the colour which results when the washed and drained cloth is put into the dye-beck, is often devoid of lustre and very subject to alteration, apparently, because the quantity of mordant on the cloth is too small to form an intimate combination with all the colour which is deposited. On applying, however, either the same mordant a second time, or else another mordant, the brilliancy of the tint is greatly increased, and the colouring material becomes permanently attached. The second mordant which is applied in this manner is known among dyers by the name of *alterant*, proposed by Dr. Bancroft. A particular example will render such a process more intelligible. If a piece of white cotton cloth is transferred at once from a dilute solution of perchloride of tin to a weak decoction of logwood, the cloth assumes an uneven violet colour, feebly attached and removable by washing. But if the perchloride remaining on the surface is thoroughly removed before the cloth is put into the decoction, the piece assumes a dull brownish violet tint ; by properly adjusting the strength of the solution of perchloride to that of the decoction, the latter may be entirely deprived of colour. If, in the next place, a small quantity of a solution of perchloride of tin, or acetate of alumina, is added to the liquor as an alterant, the cloth acquires a good violet or purple colour, and is now permanently dyed.

The most probable explanation of the action of the alterant in such a case as the above, is the following. With a proper proportion of the colouring matter of logwood, peroxide of tin forms a compound possessed of a lively colour, which compound is capable of uniting loosely with more of the colouring matter of logwood, the proper tint of which, by itself, is red. The colouring matter in excess does not partake of the lively violet or purple tint, of what may be considered as the neutral compound with the mordant, but the effect of applying more mordant (as the alterant) is obviously to form a neutral compound with the excess of colouring matter possessing the proper violet or purple colour. If the decoction of logwood to which the mordanted and washed cloth is exposed, is mixed with a very small quantity of a free acid, the precipitation of an excess of colouring matter is prevented (partly, it would seem, through the solvent power of the acid); so that the cloth assumes a lively colour at once, and the application of an alterant is unnecessary.

It is not essential to the character of an alterant that its action partake of that of a mordant. Thus, instead of mixing a free acid with the decoction of logwood, the acid may be afterwards applied to the dyed cloth, in which case it becomes the alterant, partly by removing some of the colouring matter in excess, and partly by disintegrating the particles of the mordant, whereby the latter is enabled to form a more intimate combination with the colouring matter.

In an extended sense, the term alterant may be applied to any substance which can effect a permanent change in the colour of a dyed cloth, whatever may be its chemical action. Thus, oxalic acid becomes an alterant when applied to the purple woollen cloth obtained by cochineal with a mordant of protoxide of tin, whereby the purple becomes changed to scarlet; bichromate of potash may also be called an alterant when applied to a piece of cotton dyed violet with log-wood and alumina, in order to change the violet into a black.

In a few cases, where the affinity of the colouring matter for a mordant is not sufficiently strong for the former to separate, by itself, the mordant from the substance with which it is already in combination, the solution of the mordant and that of the colouring material may be mixed without the formation of a precipitate. Thus no precipitate of colouring matter and mordant ensues when the soluble combination of alumina and caustic potash (aluminate of potash) is mixed with a solution of the colouring matter of annatto; nor when a solution of protochloride of tin is added to a *cold* decoction of logwood. When this is the case, the cloth is not always first impregnated with the mordant and afterwards with the colouring matter, but both may be applied at once by exposing the cloth to the mixture previously made. So far as the mere operation is concerned, however, this style of dyeing differs from that we have been considering, being referable to the third style according to the division followed in this section (page 262); but the function of the mordant and its action on the dye are of precisely the same nature as when the mordant is first applied, excepting that the formation of the insoluble compound of mordant and colouring principle which attaches itself to the fibre, appears here to be partly determined, as an induced effect, by the surface attraction of the tissue for the resulting compound. A similar effect may be produced in the above mixture of protochloride of tin and decoction of logwood by the application of heat, which seems to increase the mutual affinity of the mordant and colouring principle. The cloth does not in such cases abstract the whole of the colouring matter from the dyeing liquor, but the depth of its colour corresponds, in general, to the strength of the infusion, the temperature, and the time during which it is exposed to the mixed liquid.

Vegetable colouring matters are not often applied to goods of cotton by this style of dyeing except as steam colours, where the mixed solution of mordant and colouring matter is printed on the cloth, and the fixation afterwards effected by exposure to steam. The principal colouring principles thus applied are those of logwood, French berries, cochineal, peachwood, and quercitron, with a tin or aluminous mordant: an orange colour is sometimes imparted to cotton by means of the mixture of annatto and alumina in caustic potash, applied as above.

It rarely happens that the common aluminous mordants, such as basic alum and red liquor, can be employed alone as mordants for vegetable colouring matters when applied as steam or topical colours, on account of the facility with which the alumina is precipitated by the vegetable decoctions. But this tendency to precipitation may be greatly diminished by applying to the alumina a more powerful solvent. Thus, the solutions of alumina commonly employed with logwood, &c., when applied as steam colours, are basic alum mixed with oxalic or another strong acid, red liquor mixed with oxalic acid, and common alum mixed with sugar.

As the combination of the colouring principle with the mordant is to be considered a case of true chemical union, it might be anticipated that the colouring matter often experiences a considerable modification in tint on uniting with a mordant, independent of the colour possessed by the mordant itself, consistently with the law that a change of properties always attends chemical combination. Such a change in colour is certainly often exhibited, but sometimes the colour of the resulting compound is intermediate between that of the colouring matter and that of the mordant; and the colour of the dye-liquor may generally be imparted to a tissue without much alteration by the use of a white mordant.

If a piece of cloth is impregnated with alumina and then passed through the madder-beck, it acquires a rose tint; in the same dye-beck, but with peroxide of iron as the mordant, the cloth becomes dark brown or even black; and with a mixture of alumina and peroxide of iron, a puce colour may be obtained. If three pieces of cotton, one impregnated with alumina, another with peroxide of iron, and the other with oxide of copper, are passed through a decoction of quercitron, the piece containing alumina presents very nearly the proper yellow of the dye; that with oxide of iron has a dark fawn colour, and that with oxide of copper a yellowish fawn colour. Cochineal produces a purple compound with a mordant of protoxide of tin, which is itself white;

but a scarlet compound with peroxide of tin, which is also white.

The quantity of the colouring matter absorbed by the mordanted cloth is, in general, proportional to the quantity of mordant it contains, which may be determined by the strength of the solution of the mordant. Hence two pieces of cloth impregnated with solutions of the same mordant of unequal strength would present very different depths of colour by being passed through the same dye-beck. With the acetate of iron as a mordant, the same infusion of madder may be made to afford any variety of tint between faint lilac and black, and with an aluminous mordant any shade between the most delicate pink and dark red.

The class of bodies from which mordants are derived is the metallic oxides or bases, whence they might be supposed as numerous as metals which form insoluble oxides; but so many qualifications are required in a mordant, besides insolubility, that their number is very limited. Those most commonly employed are alumina, peroxide of iron, peroxide of tin, and protoxide of tin. The chemical affinity of these bases for colouring matters has already been alluded to (page 237); and many of their salts, or compounds with acids, have likewise a considerable attraction of surface for the stuffs, so that the latter have the power of withdrawing them to a certain extent from their solutions. These bases also possess a property which seems often to be highly advantageous, namely, that of forming with the same acid, when united with it in different proportions, a soluble and an insoluble combination.

Alumina,* which is the most extensively employed of the mordants, may be applied to cloths from four different solutions; 1°, from ordinary alum, which is a double salt composed of sulphate of alumina and sulphate of potash; 2°, from the solution of subsulphate of alumina, also known as basic alum, which is merely common alum with a portion of its acid neutralized by an alkali; 3°, from red liquor, which is commonly a solution in acetic acid of the subsulphate of alumina insoluble in water; and 4°, from a solution of alumina in caustic potash, known as the aluminate of potash. From alum, from the soluble subsulphate of alumina, and from common red liquor an insoluble subsulphate is produced on the cloth containing less sulphuric acid than the soluble subsulphate; and alumina itself is deposited from the aluminate of potash.

1. *Alum.*—This salt, in its ordinary state, is not much employed at present in cotton dyeing, being superseded by basic alum, red liquor, and the aluminate of potash; but it is still extensively used in silk dyeing and printing, and is the principal mordant used in the dyeing of wool. On cotton goods common alum is sometimes employed as the mordant for topical and steam colours, where the alu-

* This earth is thrown down as a white bulky precipitate when a solution of alum is mixed with an excess of ammonia. It is not obtained pure, however, by such a process, but retains some of the sulphuric acid. To prepare pure alumina, the precipitate as thus obtained may be redissolved in dilute sulphuric acid and again precipitated by ammonia. The proper neutral sulphate of alumina is very soluble in water and difficult to crystallize; by the addition of sulphate of potash it becomes common alum, which is much less soluble and very easily crystallized.

mina is required to be held in solution pretty strongly. The chemical constitution and properties of alum will form the subject of a future paper.

The impurity which common alum is likely to contain of greatest moment to the practical dyer is *iron*, existing in the state of sulphate (usually, both of the peroxide and protoxide,) and chloride. It is derived from the mother liquor from which the alum was crystallized.

The readiest method of detecting this impurity is by adding to the aqueous solution of alum a few drops of a solution of yellow or red prussiate of potash, which cause the formation of a precipitate of Prussian blue with a very small trace of iron. The precipitate at first produced with the yellow prussiate is generally greenish-white, but becomes blue on exposing the mixture to the air for a few minutes. In this case the iron is present in the alum in the state of a salt of the protoxide; and a solution of the red prussiate, instead of the yellow, causes the immediate production of Prussian blue. If the solution of alum to be tested is first boiled with a few drops of nitric acid to convert the protoxide of iron into peroxide, Prussian blue is immediately formed on applying the yellow prussiate.

In the few processes of cotton dyeing in which alum is employed as the mordant, the strength of the solution of alum and the manner of applying it entirely depend on the nature of the dye and the depth of the colour to be produced. In most cases, where the entire surface is to be impregnated with the colouring material, the goods may be allowed to remain for twenty-four hours, or more, in a cold solution containing about one part of alum to four parts of the cloth, with as much water as is requisite to cover the cloth. Silk may be digested for from eight to twenty-four hours, or longer in a cold solution of three or four parts of alum to ten or twelve parts of silk and one hundred of water. Wool may be impregnated with alum by heating it in a solution containing of alum from one-sixth to one-fourth of the weight of the wool, and maintained at the boiling point for one hour, or a little longer; but ebullition for two hours is prejudicial. A very common addition to alum when employed as a mordant, especially for wool which is intended to be brightened by an acid after being dyed, is tartar (crude cream of tartar), which diminishes the tendency of alum to crystallize, and brightens the resulting colour. The quantity which is added varies for different dyestuffs from one-fourth to one-half of the weight of the alum. When employed as a mordant for topical or steam colours, a quantity of sugar is usually added to the alum.

2. *Basic alum.*—As common alum, of itself, has very little disposition to form an insoluble subsalt, it is a weak mordant for cotton goods, and has hence been superseded by other aluminous preparations, from which subsalts may be more easily produced. One of these is basic alum, which is made by separating from common alum a portion of its acid by the application of an alkaline carbonate. It is found that one-third of the acid contained in common alum is sufficient to retain in solution all the alumina of the alum, provided the liquid is cold and in a concen-

trated state. The partial separation of the acid may be effected either by carbonate of potash or carbonate of soda, added until it begins to produce a permanent precipitate. A gelatinous precipitate is formed from the first addition of the alkaline carbonate, but it redissolves on stirring, until two-thirds of the quantity necessary for complete saturation has been applied.* In this state alum is a powerful mordant, as the excess of base is held in solution very feebly, and is easily removed in the state of an insoluble subsulphate through the surface attraction of the tissue. Animal charcoal also readily withdraws the excess of alumina, by virtue of the same force.

A solution of subsulphate of alumina is also produced when chalk is digested in a solution of common alum, sulphate of lime being then formed. According to Hausmann, one part of alum, with the addition of one-eighth part of chalk, may be retained in solution during summer by five parts of water. One part of common alum requires between eighteen and nineteen parts of cold water for its solution.

A solution of basic alum prepared by an alkaline carbonate, as above, cannot be well employed except in a concentrated state, as mere dilution with water determines the formation of a precipitate of insoluble subsulphate of alumina. But this inconvenience may be overcome, and an excellent mordant obtained, by adding acetic acid to the solution of basic alum. The mixture thus formed, which is

* A convenient mode of preparing the solution of basic alum is to dissolve in water two-thirds of the quantity of common alum operated on, to add carbonate of soda to the solution until the mixture exhibits a slight alkaline reaction, and then to add the remaining one-third of alum with agitation.

quite analogous to common red liquor, affords no precipitate on dilution with water.

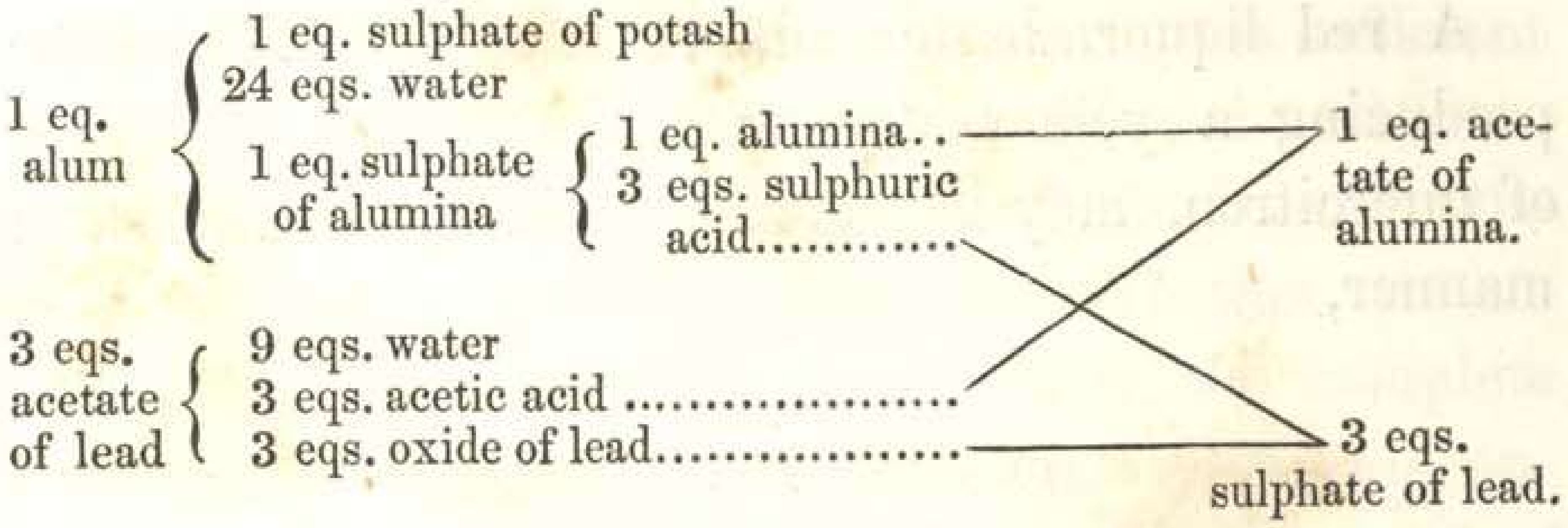
3. *Red liquor and acetate of alumina.*—Red liquor is much more extensively employed as a mordant than any other preparation of alumina. The common method of preparing this liquid for the use of the dyer and calico-printer is by adding a solution of acetate of lead or acetate of lime to a solution of alum, when a portion of the sulphuric acid of the alum combines with the oxide of lead or the lime of the acetate to form an insoluble sulphate, and the acetic acid previously in combination with oxide of lead or lime combines with alumina to form a soluble acetate. To produce complete decomposition both of the sulphate of alumina and the sulphate of potash in the alum, with formation of sulphate of lead and acetates of alumina and potash,

478 parts, or 1 eq. of alum, require
756 parts, or 4 eqs. of crystallized acetate of lead.

And for the complete decomposition only of the sulphate of alumina in the alum,

478 parts, or 1 eq. of alum, require
567 parts, or 3 eqs. of crystallized acetate of lead.

The reactions which occur on mixing solutions of these materials in the latter proportions are expressed in the following diagram:



But the quantity of acetate of lead employed in the preparation of red liquor is never greater than that of the alum, and commonly one-third less, the proportions being slightly varied according to the purposes for which the mordant is required. A small quantity of carbonate of soda (from one-twentieth to one-tenth of the weight of the alum) is also sometimes added to the mixture to separate a portion of the sulphuric acid contained in the excess of alum.

The following proportions of the materials afford a strong mordant of specific gravity about 20° Twaddell* (1100), well adapted for producing dark reds with madder:

No. 1.

5 gallons of water,
10 pounds of alum,
1 pound of soda crystals,
10 pounds of acetate of lead.

The alum is first dissolved in boiling water, and to this solution the soda is added gradually; when the effervescence is subsided, the acetate of lead is added in a state of fine powder, and the mixture having been well agitated is allowed to stand for the sulphate of lead to settle, after which the supernatant liquid may be decanted for use.

* Degrees on Twaddell's hydrometer may be converted into the ordinary sp. gr. formula (water being 1000) by multiplying them by 5 and adding 1000.

A red liquor, better adapted than the above for producing a yellow dye with the colouring matter of quercitron, may be made by mixing, in the same manner,

No. 2.
5 gallons of water,
10 pounds of alum,
1 pound of soda,
7½ pounds of acetate of lead.

In consequence of the expense of acetate of lead, this salt is commonly superseded, in the preparation of red liquor, by acetate of lime, obtained by neutralizing with quick-lime the crude acetic acid or pyroligneous acid afforded by the distillation of wood; but the red liquor thus prepared does not produce with colouring matters such delicate and bright shades as that prepared by acetate of lead. The usual proportions of acetate of lime and alum employed for this purpose are two pounds and a half of the latter to a gallon of solution of the former of specific gravity 12° or 13° Twaddell. As met with in commerce, red liquor usually has a spec. grav. about 18° Twad.

The following mode of preparing red liquor by acetate of lime is recommended by M. Kœchlin-Schouch (*Bulletin de la Société industrielle de Mulhausen*, t. i. p. 277). In twenty-five gallons of hot water dissolve two hundred pounds of alum, and to the solution add three hundred pounds of the crude solution of acetate of lime of specific gravity 16° Twad. The resulting red liquor has the density, while hot, of 22° Twad., but on cooling it deposits crystals of alum, and falls in specific gravity to 18° Twad.

In neither of the preceding preparations is sufficient acetate of lead or acetate of lime employed to decompose the whole of the sulphate of alumina in the alum, and it is doubtful, moreover, whether acetate of lime, in any quantity, would effect the complete decomposition of sulphate of alumina. But this undecomposed alum or sulphate of alumina, instead of being useless, as some have supposed, forms a highly important constituent of the mixture. By its action on the acetate of alumina in the solution, it gives rise to the formation of subsulphate of alumina or basic alum, and free acetic acid, and the latter serves to retain the former in a state of more permanent solution than water would alone.

On applying heat to red liquor, a precipitate of subsulphate of alumina is produced in the liquid, containing, according to the analysis of M. Kœchlin-Schouch, eight equivalents of alumina and three equivalents of sulphuric acid, or, eight times as much alumina as the neutral sulphate in common alum. The temperature at which the precipitation commences varies according to the strength of the liquor and the proportions of acetate of lead and alum employed in its preparation. When made as No. 1, page 281, the precipitation commences at about 154° Fahr. If the source of heat is withdrawn soon after the precipitate appears, so as to avoid the evaporation of acetic acid and the aggregation of the precipitate, the latter completely redissolves as the liquid cools; but if the heating is continued until a sensible quantity of the acetic acid is evaporated and the precipitate is become dense, the subsulphate does not redissolve on cooling, nor even on the addition of free acetic acid. Such a precipitation of insoluble subsulphate, accompanied with the evaporation of acetic acid, always occurs during the drying and "ageing" of cottons printed with red liquor.*

A solution of pure acetate of alumina obtained by dissolving recently precipitated hydrate of alumina in acetic acid is uncrystallizable, and dries, on evaporation into a gummy mass, very soluble in water. The aqueous solution of the pure acetate may be boiled without decomposition; but if a solution of alum is added to acetate of alumina, so as to form a mixture analogous to red liquor, the liquid affords, on the application of heat, a precipitate of subsulphate, of the same composition as that produced from common red liquor, which redissolves on the cooling of the liquid if the acetic acid has not been expelled.

Acetate of alumina made without excess of alum is very rarely used as a mordant, the proportions of alum and acetate of lead employed in almost all cases being four parts of the former to three parts of the latter. The chief use of the pure acetate, or rather of the mixture of pure acetate with sulphate of potash, such as is obtained by mixing eight parts of alum with nine and a half parts of acetate of lead, is to add to mixtures for topical colours containing a strong acid, such as muriatic, sulphuric, or nitric, in the free state. The strong acid combines with the

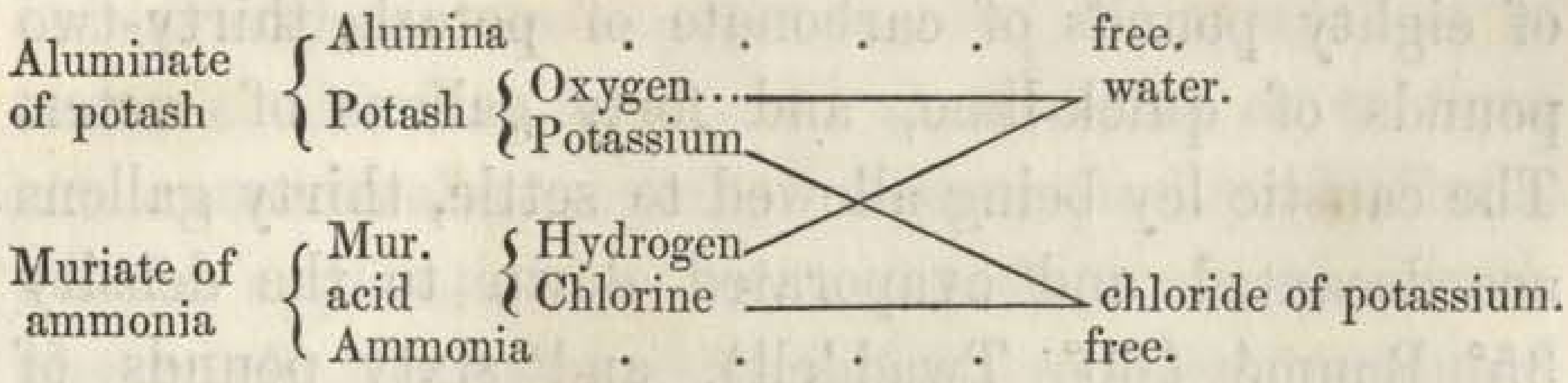
* Concentrated red liquor deposits a small quantity of the subsulphate of alumina at common temperatures, if kept for a considerable time. The precipitate thus gradually formed is sometimes too aggregated to be redissolved on the application of acetic acid.

alumina of the acetate, and liberates acetic acid, which exerts no corrosive action on the fibre of the cloth.

4. *Aluminate of potash.*—Another preparation of alumina much employed as a mordant for cotton goods, is the solution of alumina in caustic potash, known as the aluminate of potash. The following method of preparing this solution is recommended by M. Kœchlin-Schouch. A solution of caustic potash is first made by boiling for half an hour a mixture of eighty pounds of carbonate of potash, thirty-two pounds of quick-lime, and forty gallons of water. The caustic ley being allowed to settle, thirty gallons are decanted and evaporated down to the density 35° Baumé (60° Twaddell), and sixty pounds of powdered alum are added to the boiling liquid. As the solution cools, a quantity of sulphate of potash is deposited in crystals.

When a piece of cloth impregnated with the aluminate of potash is suspended freely in the air, the carbonic acid of the atmosphere seizes upon the caustic potash which holds the alumina in solution, causing the formation of carbonate of potash and precipitation of alumina. If the apartment in which cottons printed with the aluminate of potash are suspended is imperfectly ventilated, after a short time not a trace of carbonic acid can be detected in the atmosphere by the ordinary test of lime-water; hence the necessity of paying particular attention to the means of producing a proper ventilation in the "hanging" or "ageing" room, if the complete precipitation of the alumina during that stage of the process is required.

The time of hanging the mordanted goods, however, is seldom prolonged sufficiently to allow of the complete decomposition of the aluminate of potash. This is ensured by afterwards passing the cloth through a dilute solution of muriate of ammonia,* which immediately determines the complete precipitation of the alumina. The reactions which take place when a solution of aluminate of potash is mixed with a solution of muriate of ammonia are expressed in the following diagram:



The aluminate of soda may be prepared in the same manner and used for the same purposes as aluminate of potash. It is said that no difference is perceptible between the effects obtained by aluminate of potash, and those by aluminate of soda.

The other simple preparations of alumina which are occasionally used as mordants are, nitrate of alumina, chloride of aluminum, and tartrate of alumina. Of these, the most extensively employed is the nitrate, which may be prepared of sufficient purity for the use of the dyer and calico-printer by mixing concentrated solutions of equal weights of alum and nitrate of lead, when sulphate of lead is formed and

* The muriate of ammonia is sometimes mixed with the dung-beck, and sometimes with the solution of "dung-substitute." In a few particular styles of calico-printing, where the ageing of cottons printed with aluminate of potash is altogether omitted, the cloth is passed through a solution of muriate of ammonia before the dung emulsion.

precipitated, and nitrate of alumina remains in solution.

Tin mordants.—Several preparations of tin are employed as mordants in dyeing and calico-printing, comprising salts of the protoxide and of the peroxide, and mixtures of the salts of both oxides. The oxides of tin have a strong tendency to unite with soluble vegetable and animal colouring matters, producing distinct and definite combinations; and the compounds with the peroxide are generally distinguished for possessing a vivacity of tint far superior to that presented by the combinations of the same colouring matter with any other mordant.

Peroxide of tin is used as a mordant chiefly with cochineal, Brazil-wood, peachwood, barwood, French berries, and logwood, and is commonly applied in the state of a solution of the perchloride (permuriate), or as a mixture of the solution of the perchloride with that of the pernitrate. Such solutions, which are known among dyers by the name of *red spirits* or simply *spirits*, may be obtained by dissolving metallic tin, in a granulated or "feathered" state, in one of the following liquids:

1°. Aqua regia, which is a mixture of nitric and muriatic acids;

2°. A mixture of nitric acid and muriate of ammonia; and

3°. A mixture of nitric acid, muriate of ammonia, and common salt.

The perchloride of tin, or a mixture of the perchloride and pernitrate, is also sometimes prepared from crystals of the protochloride (salts of tin) by means of nitric acid or aqua regia. The nitric acid used for this purpose should be quite free from sulphuric acid.

A great number of receipts for the preparation of this mordant have been prescribed, varying very considerably in the proportions of the materials, according to the nature of the fabric to be dyed, and that of the dye-stuff for which it is to be used as the mordant. Some of the preparations contain the peroxide or perchloride only; but others, which are preferred for general use, contain both the perchloride and the protochloride. A common process for preparing a mixture of the two chlorides is to add granulated tin very gradually to a mixture of three parts by measure of muriatic acid, and one part of commercial nitric acid, so long as any tin is dissolved in the cold. If the tin is not added gradually, instead of being dissolved, it is converted into the insoluble peroxide, which is deposited as a white powder.

The above proportions answer well for a mordant for general use, and especially for Brazil-wood; but for particular purposes the proportions of muriatic and nitric acids are varied from six parts of the former, and one of the latter, to equal parts.

The solution of the perchloride of tin, or mixed perchloride and protochloride made by dissolving tin in a mixture of nitric acid and sal-ammoniac, is much used by silk and woollen dyers, but a considerable difference exists between the proportions of the materials as recommended by different dyers. For general purposes, the solution afforded by the following proportions receives a decided preference.

3 quarts of nitric acid of specific gravity 1·300,
4 quarts of water,
12 ounces of muriate of ammonia,
30 ounces of granulated tin.

The muriate of ammonia is first dissolved in the mixture of acid and water, and to this solution the tin is added in small quantities at a time, so as to prevent the mixture from becoming very hot.

The salt met with in commerce under the name of *pink salt* is the double perchloride of tin and muriate of ammonia (chloride of tin and ammonium), which is made by adding muriate of ammonia to a solution of the perchloride, and evaporating to obtain crystals. It is chiefly used as a mordant with peach-wood.

Peroxide of tin is often applied to cloth in the state of the soluble combination of caustic potash and oxide of tin, known as stannate of potash, which may be obtained by adding a solution of caustic potash to a solution of perchloride of tin, until the precipitate at first produced is entirely redissolved. If a piece of cotton impregnated with such a solution is dipped into dilute sulphuric acid, or a solution of muriate of ammonia, the alkaline combination on the cloth is decomposed, and peroxide of tin precipitated within the fibre. The decomposition which ensues on mixing stannate of potash with muriate of ammonia is quite analogous to that which occurs on the mixture of aluminate of potash with muriate of ammonia (page 286).

Protoxide of tin is frequently used as a mordant alone, as well as the peroxide. This oxide may be applied from the protochloride of tin, which is prepared by dissolving metallic tin in pure muriatic acid to saturation, with the assistance of heat. One part of tin may be dissolved in about three parts of concentrated muriatic acid, and on evaporation the solution affords small colourless crystals, distinguished as *salts of tin*. The solution of the protochloride is known among dyers by the name of *plum spirits*, being used in the preparation of the *plum tub*, which is a mixture of decoction of logwood with the protochloride.

This salt has several interesting applications in calico-printing, both as a mordant and a deoxidizing agent, to which we shall again have occasion to advert. The solution of protoxide of tin in a caustic alkali, obtained by adding the alkali to the solution of protochloride of tin until the protoxide at first precipitated is redissolved, is frequently used in the place of the protochloride.

When exposed to the air, a solution of protochloride of tin absorbs oxygen, and affords, if not very acid, a white precipitate consisting of a subsalt of the peroxide. This inconvenience may be counteracted to a great extent by the addition of muriate of ammonia which combines with the protochloride to form a double salt, less disposed to absorb oxygen than the pure protochloride.

The colours of the compounds of colouring matters with peroxide of tin are generally much brighter than those of the same compounds with protoxide of tin, but solutions of the protoxide enter the pores of cotton fabrics better than solutions of the peroxide.

On this account, a practice sometimes pursued in dyeing cotton goods by a tin mordant, is first to apply the tin in the state of protochloride, and to form the peroxide afterwards, within the fibre, by wincing the goods in a dilute solution of chloride of lime.

Iron mordants.—The principal simple preparations of iron which are employed as mordants are the following: copperas, which is the sulphate of the protoxide; iron liquor, which is an impure acetate of the protoxide; the pernitrate, the sub-persulphate, and the perchloride. The most available of these forms of iron is copperas; but this salt is not well adapted as a mordant for cotton goods, as the powerful affinity of sulphuric acid for protoxide of iron is an impediment to the formation of an insoluble subsalt.

Acetate of iron; iron liquor.—The iron mordant commonly used in calico-printing is the acetate, which may be prepared by mixing a solution of acetate of lime or acetate of lead with a solution of copperas. A double decomposition occurs on the mixture of these solutions, with the formation of sulphate of lime or sulphate of lead, which falls as a heavy precipitate, and acetate of protoxide of iron, which remains in solution. For the complete decomposition of copperas by acetate of lead, 10 parts of the former require about 13½ parts of the latter; but in the preparation of acetate of iron in this way on the large scale, the copperas is always employed in excess, being seldom in so small a proportion to the acetate of lead as an equal weight. By exposure to the air the acetate of the protoxide becomes partially peroxidized, being converted into a subacetate of the peroxide.

But nearly all the acetate of iron used in print-works is now prepared by digesting, for several weeks, old iron hoops, nails, &c., in the crude acetic acid obtained by the distillation of wood. A dark brown solution, known as the pyrolignite of iron or iron liquor, is thus obtained, composed of the acetate of the protoxide of iron, and a quantity of tarry, oily, and spirituous matters produced in the destructive distillation of wood. As a mordant, this mixture is in general preferred to the purer article prepared by means of acetate of lead or acetate of lime, probably because the peroxidation of the protoxide of iron by exposure to the air during the "ageing" of the goods is retarded by the spirituous and unctuous matters present which have a stronger affinity for the oxygen of the air. A small quantity of the acetate of the peroxide of iron is sometimes contained in iron liquor, but by no means as an essential constituent.

The principal pure persalt of iron used in dyeing and calico-printing is the nitrate, which is prepared by dissolving clean pieces of iron in nitric acid of specific gravity 1·305. Soon after the evolution of brown fumes ceases, the acid solution should be decanted, so as to avoid the formation of the insoluble sub-pernitrate of iron. This solution of iron is used as a mordant with vegetable colouring matters, and also for producing a buff colour with an alkali (see page 256), and Prussian blue with yellow prussiate of potash.

A preparation of iron extensively employed at some print-works in the place of the common acid pernitrate, is a mixture of the neutral pernitrate with free acetic acid, obtained by adding about a pound of powdered acetate of lead to two pints of a solution of the pernitrate, of the density 1·55. The acetate of lead is decomposed by the free nitric acid present in the solution, with formation of nitrate of lead, which is precipitated, and free acetic acid.

A solution of a sub-pernitrate of iron, made by adding a small quantity of an alkaline carbonate to the pernitrate, is also sometimes advantageously substituted for the pernitrate prepared as above. The peroxide of iron at first precipitated may be redissolved on agitation, if only a small proportion of alkali has been applied.

Two other forms of peroxide of iron have been occasionally employed as mordants; one analogous in its chemical constitution to basic alum (page 278), and the other to red liquor (page 280). The first is prepared by partially decomposing, by means of an alkaline carbonate, the persulphate of iron made by boiling copperas in dilute nitric acid. The oxide at first precipitated by the alkali is slowly redissolved by the undecomposed persulphate, giving rise to the subsulphate of the peroxide. The preparation of peroxide of iron, analogous to red liquor, may be made by adding one part, by weight, of acetate of lead to four parts of a solution of persulphate of iron of the density 1·65. Sulphate of lead is precipitated, and the solution comes to contain subsulphate of the peroxide of iron, and peracetate of iron or free acetic acid.

A patent has been recently obtained by Mr. Mercer and Mr. Barnes for the preparation of an acidulous liquid for mixing with ferruginous mordants, which imparts considerable brilliancy to the tints of all compounds of colouring matters (particularly that of madder) with peroxide of iron. This liquid, known as "assistant mordant," or "patent purple liquor," is made by digesting farinaceous substances, starch, or sugar, in warm nitric acid, of moderate strength. The temperature of the mixture is not allowed to become high, in order to prevent the formation of oxalic acid. When all the nitric acid present is decomposed, a little pyroligneous acid is added, and the mixture is then ready for use.

For producing a black die, with oxide of iron and madder, one measure of iron liquor may be mixed with one or two measures of "assistant;" for light purples, the proportion of "assistant" may be increased to five or six measures. The beneficial action of this preparation is considered to consist chiefly in the retardation of the peroxidizement of the iron mordant during the "ageing."

The enlivening action of strong acids and acidulous salts on the tints of some vegetable and animal colouring matters, when applied in a diluted state to the compounds of colouring matters and mordants, is a subject which deserves the particular attention of the dyer and calico-printer. Instances of this effect of the application of acids, either to the dyed cloth or to the infusion of the colouring matter, are of frequent occurrence ; and some bright shades of colour cannot be obtained without the assistance of an acid, though the mode of action of the acid is by no means obvious.

If a piece of cotton is printed or padded with iron liquor, dunged, winced in a mixture of chalk and hot water, and then dyed in a decoction of *valonia* or other vegetable matter containing tannin, it acquires merely a dull drab colour. But if the cloth thus dyed is exposed for a short time to the fumes of hydrochloric acid, or if winced in very dilute sulphuric or hydrochloric acid, the colour of the cloth changes from drab to slate colour or black, according to the quantity of mordant on the cloth. Acetic acid produces the same effect, but not in so powerful a manner as sulphuric acid, of which a mere trace is as effective as a much larger quantity. The colour of the compounds of both oxides of tin (but especially that of the protoxide) with the colouring matter of logwood may also be greatly enlivened by the application of very dilute sulphuric acid, and a good scarlet or crimson cannot be obtained from cochineal with a tin or aluminous mordant without the introduction of tartaric or oxalic acid or cream of tartar.

That the mode of action of the acid in such cases varies with different colouring matters and mordants hardly admits of doubt. The quantity of acid required in some cases is far too small to warrant the supposition that it enters into a permanent chemical union with the colouring matter and mordant; but in other cases a sensible quantity of acid disappears, and seems to enter as an essential constituent into the composition of the colouring material.

In cases where the acid does not enter into a permanent chemical combination with the mordant and colouring matter, it may be considered to act in two ways:

1. By preventing the deposition of an excess of the colouring matter on the mordanted cloth, or by removing such an excess, if already deposited, through its solvent power;

2. By effecting the disintegration of the particles of the mordant, whereby the latter is enabled to form a more intimate combination with the colouring material.

When a piece of cotton cloth impregnated with a mordant in the ordinary manner is immersed in the dyeing decoction, it often absorbs more colouring matter than is necessary to form what may be considered as the neutral compound of colouring matter and mordant. But this excess of the colouring principle is frequently prejudicial to the tint of the compound of the mordant with a smaller proportion of colouring matter, with which the excess is in a state of loose combination, being held, probably, by a mere attraction of surface (see page 237), and not by chemical affinity. Thus the compounds of both oxides of tin with an excess of the colouring matter of logwood are considerably inferior in vivacity of colour to the compounds of the same oxides with a smaller proportion of the colouring matter. The dulness of the colour of a piece of cotton mordanted with iron liquor, dunged, winced in hot chalky water, and dyed in a decoction of valonia (see page 295), may be attributed to the deposition of an excess of tannic acid (which is the astringent principle of the valonia) on the neutral and darker coloured tannate of iron.

Now one effect of the application of a small quantity of a strong acid to the decoction of the dye-stuff, may be the prevention of the attachment of this excess of colouring matter to the mordanted cloth; an acidulous liquid being generally a more powerful solvent of the colouring principle than pure water; and a corresponding effect may take place when the dyed cloth containing an excess of colouring matter is exposed to an acidulous liquid, the excess being then partly removed from the cloth, through the solvent power of the acid.

But a more important effect to be attained by the application of an acid is the disintegration of the mordant on the cloth, whereby the interior particles of the mordant become placed in a better condition for combining with and retaining the colouring matter. During the drying of a mordanted piece of cotton, the mordant always becomes more or less aggregated; and if the cloth is exposed to a high temperature, the aggregation may become so great with some mordants that very little colouring matter is absorbed when the cloth is immersed into the dyeing liquid containing no free acid. A remarkable difference may be observed between the quantity of the colouring matter of logwood absorbed by a piece of cotton impregnated with either perchloride or protochloride of tin, and dried at a very gentle heat, and the quantity of the same colouring matter absorbed by a piece of cloth containing the same mordant, but dried at as high a temperature as the cloth will well support. Even two pieces of cotton containing similar quantities of the same tin mordant, both dried at a low heat, but one washed in cold water after being dried, and the other in hot water, present a very sensible difference in shade when dyed in the same infusion of logwood. It is difficult to conceive how such effects are produced, except through differences in the state of aggregation of the mordant on the cloth.

But the addition of a small quantity of sulphuric acid to the dyeing liquid, causes the production of an uniform and bright colour in both pieces of cotton, whether dried at a high or low heat, or washed in hot or cold water. A mere trace of acid is generally sufficient to produce this effect, hence it cannot be supposed to act in all cases by forming a permanent chemical combination with the colouring material.

The disintegration of the precipitated mordant on the cloth seems to be the principal effect of the application of an acid in such cases as those now under consideration. The interior, uncombined, particles of the mordant thereby become exposed, and placed in a condition to unite intimately with the colouring material, the latter being derived either from the dyeing liquor or from the excess in loose combination with the exterior particles of the mordant. The disintegration of the mordant by the acid may possibly be a mere mechanical effect,* independent of any chemical alteration of the mordant, but the action of the acid admits of a more satisfactory explanation. The precipitated mordant is probably first dissolved by the acid, but is immediately reprecipitated in intimate combination with the colouring matter; the acid thereupon becomes liberated, and enabled to act in the same manner on other portions of the mordant. Whether the acid be mixed with the dyeing infusion, or applied as an alterant (see page 270) to the dyed cloth containing an excess of colouring matter, its action is of the same nature. An illustration of this principle is afforded by an experiment before referred to, which consists in exposing to the diluted fumes of muriatic acid a piece of cotton, with oxide of iron as the mordant, died to a drab colour in infusion of valonia (see page 295). The tannin or the astringent principle of the valonia is united only with the exterior particles of the oxide of iron, but is there contained in excess; on the application of the acid both the excess of tannin and the interior particles are dissolved, brought into contact, and precipitated in intimate combination, the muriatic acid being liberated to act on other portions of oxide of iron and tannin in a similar manner.

The preceding explanation of the enlivening ef-

* Examples of the disintegration of precipitates, by being digested in an acid liquid, which exerts no chemical action on the precipitates, are by no means rare. Thus, an intimate mixture of pure Prussian blue with hydrochloric acid appears to become a perfect solution on standing; but the particles of the pigment are merely disintegrated, and still exist in an insoluble form.

fects produced by the application of acids to compounds of organic colouring matters and mordants, refer only to those cases in which the quantity of acid sufficient to produce the effect is too small to warrant the supposition that it enters into a permanent chemical combination with the colouring material. In other cases a sensible quantity of free acid unites with the compound of mordant and colouring matter, and modifies the properties of the latter by causing a new disposition of its particles.

That the purple compound of the colouring matter of cochineal with protoxide of tin, for example, is capable of uniting with free sulphuric acid appears evident from the following experiment, communicated to me by Mr. Mercer. When a solution of protochloride of tin is added to a decoction of cochineal, a purple lake is precipitated, consisting of a compound of the colouring matter of cochineal with protoxide of tin mixed with an excess of the protoxide. This lake is collected on a filter, carefully washed with distilled water, and digested in a given quantity of a solution of carbonate of soda of known strength. The proper compound of colouring matter and oxide of tin then dissolves in the alkaline carbonate, and the excess of oxide of tin remains undissolved. On mixing an excess of sulphuric acid with the alkaline solution the pure lake is reprecipitated of a much richer colour than before being thus treated; but the reprecipitation of the pure lake requires considerably more acid than is necessary to neutralize the alkali. None of the lake is thrown down if no more acid is applied than the quantity exactly necessary for the neutralization; but on adding more, the precipitation immediately commences, though no free acid can be detected in the mixture until the lake is completely thrown down.

It is difficult to determine, precisely, the nature of the modification which colouring matters, or compounds of colouring matters and mordants, experience by combining with an acid in such a case as the preceding; some considerations on this subject, however, may not be without a practical application in the operations of the dye-house.

Soluble vegetable and animal colouring matters have the property of uniting both with acids and bases: with acids they form feeble combinations possessed of lively tints ; but with bases they afford stronger combinations, having less vivacity of colour. In general, the more closely a mordant resembles an acid in its chemical character, the brighter are the tints of its compounds with colouring materials. Thus, peroxide of iron and peroxide of tin, which appear to act the part, sometimes, of feeble acids, produce compounds with colouring matters having brighter colours than similar compounds with protoxide of iron and protoxide of tin. But metallic protoxides, which possess a greater basic power than their corresponding peroxides, generally form more intimate combinations with soluble organic colouring materials, than the peroxides, especially if the protoxide is of itself a stable substance, as protoxide of tin. Some metallic protoxides also unite with a large quantity of colouring matter than peroxides, but it is uncertain whether the excess is held by chemical affinity or by a mere attraction of aggregation dependent on the state of the surface of what we may consider as the neutral compound of colouring matter and mordant.

For tissues which can combine with and retain strong acids without injury to the fibre, as wool and silk,* protoxide of tin is as suitable a mordant as the peroxide, because the brightening effect which the mordant fails to produce may be obtained by the application of an acid. For this purpose oxalic acid is frequently applied to woollen goods containing protoxide of tin as the mordant.

But as very few strong acids can be applied to cotton goods without weakening the fibre to a greater or less extent, it becomes necessary, in order to obtain bright colours, to apply such mordants only as possess some resemblance to acids, as alumina, and the peroxides of iron and tin. In the action of such bodies on soluble organic colouring materials two forces may be recognized: by one, the mordant acts as an acid, producing an enlivening of tint; by the other it acts as a base, producing an intimate and stable combination.

* If silk and wool are digested in dilute sulphuric or muriatic acid, a portion of the acid combines with the stuffs, and the liquid is found weaker after than before the immersion. The animal tissues also combine with tartaric acid when digested in a solution of cream of tartar (bitartrate of potash), leaving neutral tartrate of potash behind. But cotton exhibits no such disposition to unite with acids, and when digested in dilute sulphuric or muriatic acid, abstracts the water in preference to the acid, thus making the liquid more acid than before the immersion of the cotton.

DUNGING.

As the precipitation of the mordant in the form of an insoluble subsalt during the hanging or "ageing" of cotton goods is never complete, it becomes necessary to remove the unprecipitated mordant from the cloth before the dyeing, else a quantity of superfluous colouring matter will be deposited on the surface of the cloth, which would have to be removed by subsequent operations, besides causing an unnecessary impoverishment of the dyeing liquid. But the necessity for removing the superfluous mordant is chiefly experienced with cotton goods on which the mordant is printed so as to produce a pattern. If all the mordant which remains in a soluble form is not completely removed from such goods, a portion of it may become distributed over the whole surface of the cloth when the pieces are washed in water or put into the dye-beck.

One process for effecting the complete removal of the unprecipitated mordant consists in simply drawing the dried goods through a warm emulsion of cow-dung and water. The emulsion is usually contained in two stone cisterns, each about six feet long, by three feet wide and four feet deep: that in one cistern contains about two gallons of dung, to the cistern-full of hot water; that in the second contains only half this proportion of dung. The cloth, on being taken from the "ageing" room, is first drawn pretty quickly through the emulsion containing most dung, and immediately afterwards through the other; the cisterns being usually placed end to end, to allow the cloth to be conducted directly from the first to the second. The cloth is guided in its passage through the cisterns by four or five rollers placed at each end, it being essential to the success of this operation that the pieces should be extended and free from folds. Immediately on issuing from the second cistern, the cloth is passed over the reel of a contiguous wince-pit (see figs. 31, 32, page 314), where it is well washed in clean water, and from the wince-pit it is generally taken to the dash-wheel. If the mordant on the cloth is the aluminate of potash, some muriate of ammonia is added to the dung emulsion, to ensure the precipitation of alumina, which it effects by a reaction explained at page 286. Occasionally, the cloth containing aluminate of potash is passed through a solution of muriate of ammonia before it is exposed to the dung emulsion.

In calico-printing, the dunging process is necessary for all kinds of aluminous, iron, and tin mordants, when applied to the cloth before the colouring matter. The time of immersion, the temperature of the mixture, and the number of pieces which may be passed through a given quantity of dung and water, depend entirely on the state and quality of the mordants, and on the nature of the thickening paste by which the mordants are applied. A piece of cotton with a mordant which has a strong acid requires a longer time than a piece the mordant on which has a weak acid; and when the thickening paste for a mordant is flour or starch, a higher temperature is required than when British gum or common gum is used. The usual temperature of the dung emulsion is 160° or 180° Fahr.

Dunging is one of the most important steps in the process of calico-printing; and if badly performed, especially when the mordant on the cloth is alumina, the success of the subsequent dyeing is sometimes greatly endangered. The operation has for its object, not merely the removal of the superfluous mordant, and in printed goods of the thickening paste by which the mordant is applied, but the determination of a more intimate union between the mordant and the stuff, which it seems to effect by converting the sparingly soluble subsalts on the fibre into other compounds, perfectly insoluble.

Although the objects of the operation of dunging are sufficiently obvious, yet the precise manner in which they are attained is involved in some uncertainty. According to an analysis by M. Penot, cow-dung contains the following ingredients in 100 parts.

COMPOSITION OF COW-DUNG.

Woody fibre	26·39
Albumen	0·63
Chlorophyl	0·28
A sweet substance	0·93
A bitter matter	0·74
Chloride of sodium	0·08
Sulphate of potash	0·05
Sulphate of lime	0·25
Carbonate of lime	0·24
Phosphate of lime	0·46
Carbonate of iron	0·09
Silica	0·14
Water	69·58
(Loss	0·14)
	100·00

It is generally admitted that the superfluous or unprecipitated mordant is immediately dissolved by the hot water; but instead of remaining in a state of solution, it is entirely precipitated in an insoluble form, partly by the albuminous constituent of the dung, partly by the phosphate and carbonate of lime, and partly by the insoluble ligneous fibre, and is therefore rendered incapable of attaching itself permanently to the cloth. But it appears that a small portion of the superfluous mordant dissolved from the cloth by the hot water, instead of being afterwards precipitated, is permanently retained in solution in a peculiar state of combination with the animal matter of the dung; one of the characters of which combination is, that it is incapable of affording a precipitate of subsalt or oxide to the cloth. The precise nature of this compound of the mordant with organic matter is not known, but it is believed to be analogous to that of several soluble combinations of metallic oxides with organic matters which are not affected by certain chemical reagents in the same manner as ordinary salts of such oxides. Thus, a salt of the protoxide of copper in the presence of several organic substances, sugar for instance, is not precipitated by a solution of a caustic alkali; the double tartrate of the peroxide of iron and potash does not afford a precipitate of peroxide of iron when mixed with a solution of caustic potash, nor does it yield a subsalt to cotton, like most other ferruginous salts.

The constituents of the dung which appear to be principally concerned in the fixation of the mordant on the cloth are the albuminous and soluble vegetable matters and the phosphate of lime. The former act partly by uniting with the base of the subsalt on the cloth, liberating its acid and forming a new combination more insoluble than the previous subsalt. The liberated acid may soon be detected in the liquid by the test of blue litmus paper, and requires to be neutralized, in a few processes, by the introduction of chalk.* The albuminous matter of the dung seems also to exercise an influence as a detergent or an emollient, whereby it considerably facilitates the detachment of the loosely combined mordant.

The action of the phosphate of lime in the dung emulsion is to cause the formation on the cloth of phosphate of alumina or phosphate of iron by a double decomposition, the acid in the subsalt uniting at the same time with the lime of the phosphate. Both phosphate of iron and phosphate of alumina are quite insoluble in water, and also in acetic acid, if warm.

Within the last few years the dung emulsion has been superseded, either partially or entirely, in all well-conducted print-works in this country, by a solution of phosphate of soda and phosphate of lime, known by the name of "dung substitute," or simply "substitute," for the preparation of which a patent

* On the Continent, it is a common practice to add to the dung emulsion, in all cases, either chalk or bicarbonate of soda, the latter being preferred; but it is unusual in this country to make any such addition to the dung, except in cases where the cloth contains a free acid or acidulous salt, as lemon-juice or bisulphate of potash. The smallest excess of an alkaline carbonate should be avoided when alumina is the mordant on the cloth.

has been obtained by Mr. Mercer, Mr. Prince of Lowell, Massachusets, and Mr. Blyth. A solution of an alkaline arseniate had been long previously used as a substitute for dung by Mr. Mercer.

Dung substitute is prepared by mixing sulphuric acid with bone-earth, which consists chiefly of phosphate of lime; the acid not being applied in sufficient quantity to decompose the phosphate of lime entirely, but to produce an acid phosphate, or a solution of the phosphate in free phosphoric acid. Carbonate of soda is then added to neutralize the free acid completely, and the mixture is evaporated until the residuary mass becomes almost dry. When the concrete thus obtained is mixed with water, it affords a solution of phosphate of soda containing some phosphate of lime; a white mud remains undissolved, consisting of sulphate, carbonate, and a little phosphate of lime, which should be carefully stirred up when the liquid is about to be used.

This preparation is not, of itself, an efficient substitute for all the essential, or at least for all the important, constituents of the dung emulsion. To supply an emollient and detergent substance in the place of the albuminous matter of the dung, it is found necessary to mix with the above liquid a solution of glue or some other form of gelatine. The material employed for this purpose in most print-works is a solution of bone-size, called "cleansing liquor," which is made by boiling bones in water for nearly a week, separating the fat which rises to the surface of the liquid, and evaporating the aqueous solution of gelatine until it attains a density about 36° Twaddell (1·180). The advantage of making this addition to the phosphates was first pointed out by Mr. Mercer.

When the "aged" cloth is passed through a mixed solution of substitute and gelatine, the latter greatly facilitates the separation of the loosely combined mordant, and prevents its re-attachment, while the phosphate of lime and phosphate of soda in the former serve to fix the alumina and oxide of iron in more intimate combination with the stuffs by converting them into phosphates. The acids previously in combination with the alumina and oxide of iron (when these bases existed as subsalts) unite at the same time with the soda and lime of the substitute.

The following detailed account of the best mode of applying the solution of substitute to mordanted goods has been communicated to me by Mr. Mercer. It refers to cases in which dung is entirely dispensed with, and in which the mordant is applied to the cloth topically.

The cloth is exposed to the action of two solutions of the substitute consecutively; that first applied, which is considerably stronger than the other, may be contained in a common dung cistern capable of holding not less than six hundred gallons, and furnished with a series of rollers so as to allow the immersion of fifteen yards of cloth at the same time. The weaker solution of substitute is applied to the cloth in a wince-pit.

A normal solution of substitute, called "substitute liquor," is first made by dissolving the substitute in warm water at the rate of two pounds to the gallon. Six gallons of this substitute liquor and two gallons of the cleansing liquor are introduced into the cistern, which is then filled with hot water, and the pieces of cloth are passed through at the rate of thirty yards per minute. The temperature of the solution may be the same, in general, as that of the dung-beck, in the common dunging process: for madder purples and pale reds it should never exceed 140° Fahr., but for madder blacks and full reds it may be a little higher. This cistern requires to be frequently renewed by the addition of fresh quantities both of substitute liquor and cleansing liquor. A gallon of the former and a quart of the latter may be added for every thirty or fifty pieces, according to the "heaviness" of the work, or the quantity and strength of the mordant on the cloth.

When removed from the first cistern, the pieces are well washed in water;* after which, they are winced in the weaker solution of substitute. This solution may be contained in a wince-pit or cistern capable of holding about three hundred gallons, with which quantity of hot water there should be mixed two quarts of substitute liquor and one quart of cleansing liquor. In this liquid twenty-eight or thirty pieces are winced for twenty or twenty-five minutes, at a temperature about 10° lower than the solution first applied. The second cistern requires to be renewed by the addition of two pints of substitute liquor and one pint of cleansing liquor for every twenty-eight pieces. Both this and the first cistern should be fresh charged every morning, and emptied at night.

* If the work is heavy, it is also recommended to pass them between the squeezing rollers and again wash them in water.

The only remaining operation to which the pieces are subjected, previous to being dyed, is a thorough washing in water; and if the work is heavy, they should also be passed between the squeezing rollers, and again washed.

Where the use of dung is only partially superseded by that of the substitute, the pieces are sometimes first passed through the common dung emulsion and afterwards winced in a weak solution of substitute mixed with cleansing liquor or glue: or the pieces may be first passed in the ordinary manner through a mixture of half the usual quantity of dung with half the above proportions of substitute liquor and cleansing liquor, and be afterwards winced in a solution of substitute of the same strength as the second, applied as above without any dung. For madder reds, the mixture of dung and substitute seems to be more advantageous than substitute or dung alone; but for madder purples and black, a preference is given to the use of the substitute only.

The exposure to dung or substitute of cloths mordanted with alumina, should not be prolonged a sufficient time to allow of the union of the alumina with a full proportion of phosphoric acid; for colouring matters do not readily displace phosphoric acid from such a combination. The phosphate of iron, on the contrary, is easily decomposed by colouring matters.

In a few dyeing processes where it is of importance to avoid the aggregation of the particles of the mordant as much as possible, the pieces, instead of being exposed to dung or substitute, may be winced in a mixture of chalk and size with hot water. In this case, the chalk serves to fix the mordant on the cloth by withdrawing the small quantity of acid remaining in the subsalt; and the loosely combined mordant separated by the water is precipitated by the chalk, and thus rendered incapable of attaching itself to the fibre. If the goods contain an aluminous mordant, the process of wincing in chalky water should not be prolonged, and only a small proportion of chalk should be employed, as the precipitated alumina itself is apt to be removed by the action of an excess of chalk.

The dunging process is sometimes superseded by the operation of *branning*, which consists in wincing the goods in a mixture of bran and hot water. The action of bran is probably quite analogous to that of dung, the unprecipitated mordant dissolved by the water being separated from the liquid by the insoluble ligneous matter, while the undissolved mordant becomes more strongly attached to the cloth by combining with the mucilaginous and glutinous matters present, and also with the phosphoric acid of the phosphate of lime in the bran. The only cases in which branning is preferred to dunging are those in which the cloth is afterwards dyed to delicate shades of colour by means of cochineal and fugitive colouring matters.

After having been thus exposed to the action of either dung, substitute, chalk, or bran, the mordanted goods are ready to be exposed to the infusion of the dye-stuff; and, in general, the sooner this is done, the better is the colour they assume.

The different vegetable colouring matters vary so considerably in properties, that few observations of general application can be offered on the modes of preparing the various dyeing liquids. If the substance is very soluble, its solution may be made in the cold; but if only slightly soluble, heat may be applied, provided the colour is not deteriorated by exposure to a moderate heat. When a highly charged solution is required, (such as the topical and steam colours used in calico-printing,) concentration by evaporation is had recourse to; many vegetable colours, however, will not support a continued ebullition without losing something of their colour. If the goods are not kept in constant motion when in the dye-beck, the infusion should be freed from the insoluble ligneous matters by decantation or filtration; in some cases this operation may be avoided by enclosing the tinctorial matters in bags, which are withdrawn from the liquid when sufficient colour is imparted. But if the goods are kept in continual motion in the vegetable infusion, as is almost always done with cottons, the separation of the insoluble matters is unnecessary. The vegetable material is commonly introduced in a state of coarse powder into the dye-beck containing cold water; the pieces of mordanted cotton to be dyed are put in at the same time, and the temperature of the liquor is gradually increased by the introduction of steam.

In the dyeing of cottons, motion may be communicated to the goods, while in the dye-beck, by a wince or reel placed horizontally over the middle of the dyeing vessel, so that the cloth may be made to descend into either compartment of the dye-beck by the rotation of the reel. The dyeing vessel, which is commonly constructed of wood,* is represented in cross and longitudinal section at figs. 31 and 32:

Fig. 31.

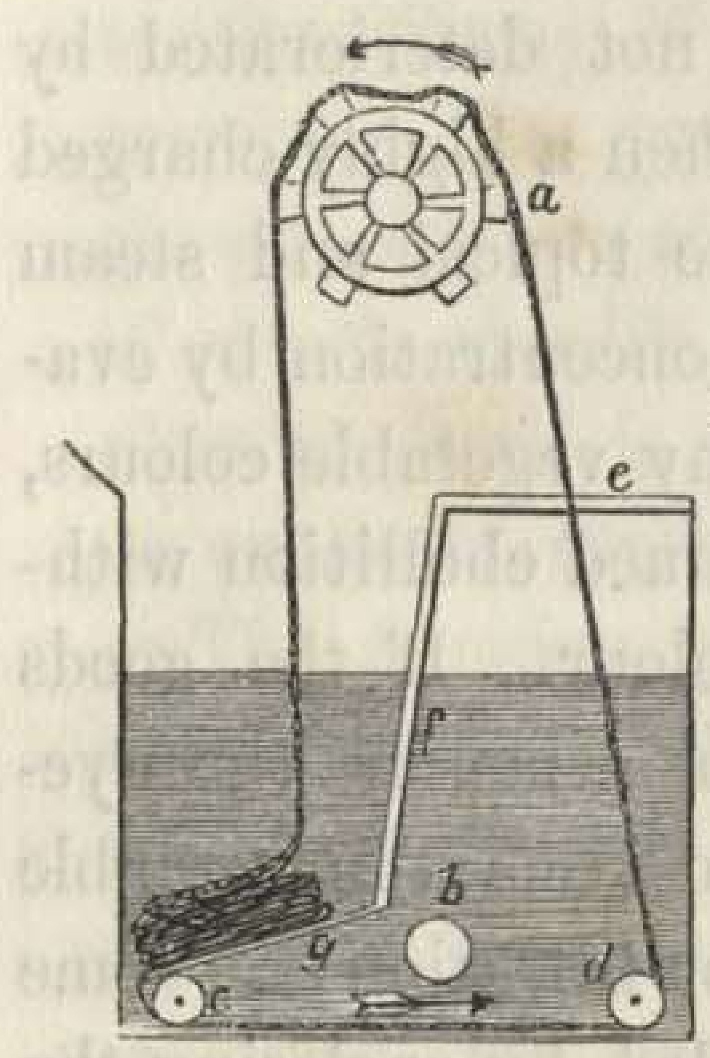
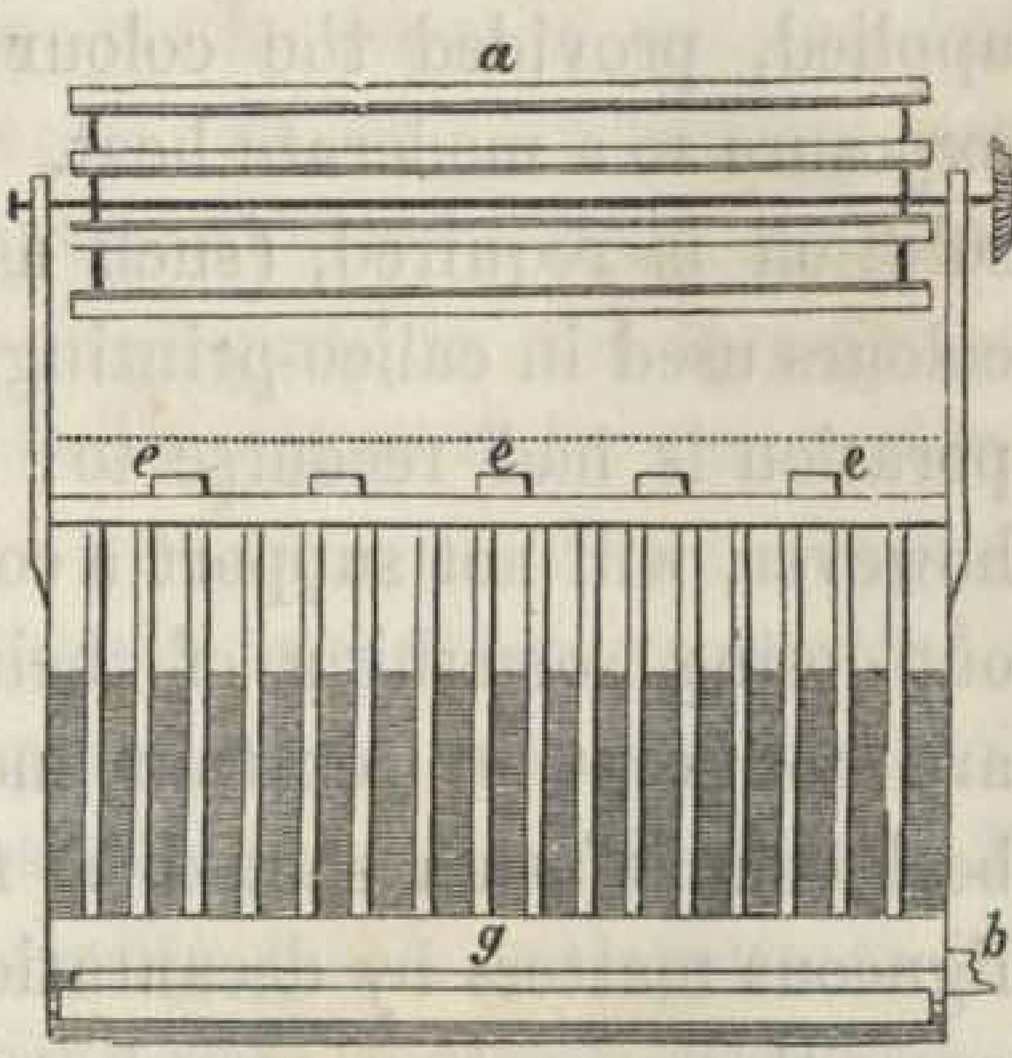


Fig. 32.



a is the reel, containing six long wooden spars on its circumference; it is set in motion by being connected with one of the driving shafts of the factory. Steam is admitted to the vessel by the pipe *b*, the upper surface of which has a great number of small perforations. Twelve, eighteen, or twenty-four pieces of cotton, which are stitched together at their ends so as to form one endless web, pass over the reel in the direction of the arrows, and fall on a sloping iron ledge *g*, on one side of the vessel, from which they pass under the two rollers *c* and *d*. Four, five, or more of such endless webs may be set in motion by the same reel, they being prevented from entangling by wooden bars represented at *e*, which

* For madder work, dye-becks made of iron have been lately substituted for those of wood. When the metal is completely covered with oxide, it exerts no injurious action on the colouring matter.

reach from a cross-bar at the top of the vessel to the back. An inclined partition, *f*, extends through the whole length of the dyeing vessel, formed of several wooden spars placed a few inches apart from each other. The ordinary dimensions of the dyeing vessel are, six feet in length, four feet in width, and four feet in depth.

Such is a general view of the course of operations practised in the dyeing of goods with colouring matters which are naturally soluble in water, by the intervention of a mordant. If the colouring principle is insoluble in water, the mordant may be dispensed with; but it then becomes necessary to devise some means of obtaining such a solution of the colouring substance as will allow the deposition of the latter in its insoluble state, when a cloth impregnated with the solution is exposed to some chemical agent. This forms the third style of dyeing in the classification proposed at page 262. The principal insoluble vegetable colouring materials are indigo, safflower, and annatto, the nature of the processes for applying which to cloth has already been explained (page 243).

The only other style of dyeing which remains to be noticed is entirely different from either of the preceding; it is practised only on goods formed of the animal tissue, and admits of no more than one example in illustration. By this style, an orange colour is imparted to silk and wool, not from the solution of a colouring matter, but by effecting a certain chemical change in the fibre, through the action of dilute nitric acid. The orange colour is due to a substance formed by the decomposition of a portion of the silk or wool itself by the acid.

The temperature of the dye-beck at the time of dyeing depends almost entirely on the nature of the colouring matter. If it is readily attachable to the tissue, as indigo and colouring principles derived from metallic substances, for instance, and if easily altered by heat, as safflower, the dyeing solution may be used cold. But a hot liquid generally affords the most uniform colour, partly on account of the more ready disengagement of air-bubbles from between the fibres of the cloth. Dyeing with vegetable and animal colouring matters which require a mordant is also effected more rapidly with the assistance of heat, owing to the increased disposition of the mordant to unite with the colouring principle. In a few dyeing processes, however, where the mordant exists on the cloth in a soluble state when about to be dyed, a high temperature in the dye-beck is injurious, from the separation of a portion of the mordant from the cloth by the solvent action of the dyeing liquor. Hence it is that cotton, silk, and flax, impregnated with alum, absorb more colouring matter from some solutions at the ordinary temperature than at the boiling point. Where the operations are conducted on anything approaching a considerable scale, the most convenient and the most economical source of heat for the dye-beck is steam, which may be applied in three ways: 1°, by introducing it directly into the liquid by a pipe leading from the boiler; 2°, by causing it to circulate through a spiral pipe placed in the dye-beck; and 3°, by introducing it between the dye-copper and an exterior wooden case.

The vessels in which the dyeing decoctions are made and concentrated by evaporation, are usually of copper; for some delicate dyes, when a steam heat is applied, they are made of tin or of copper tinned inside. Copper boilers sometimes exercise considerable influence on the tints of the decoctions prepared in them, owing to the solution of some oxide of copper from the surface of the metal, by an acid existing either in the mordant or the dye-stuff. A solution of alum which has been boiled for some time in a copper vessel affords, with ammonia, a blue instead of a white precipitate; and wool acquires a greenish-grey tint when kept for some hours in a boiling solution of alum with cream of tartar contained in a copper vessel, which would not happen with the same solution in a vessel of tin.

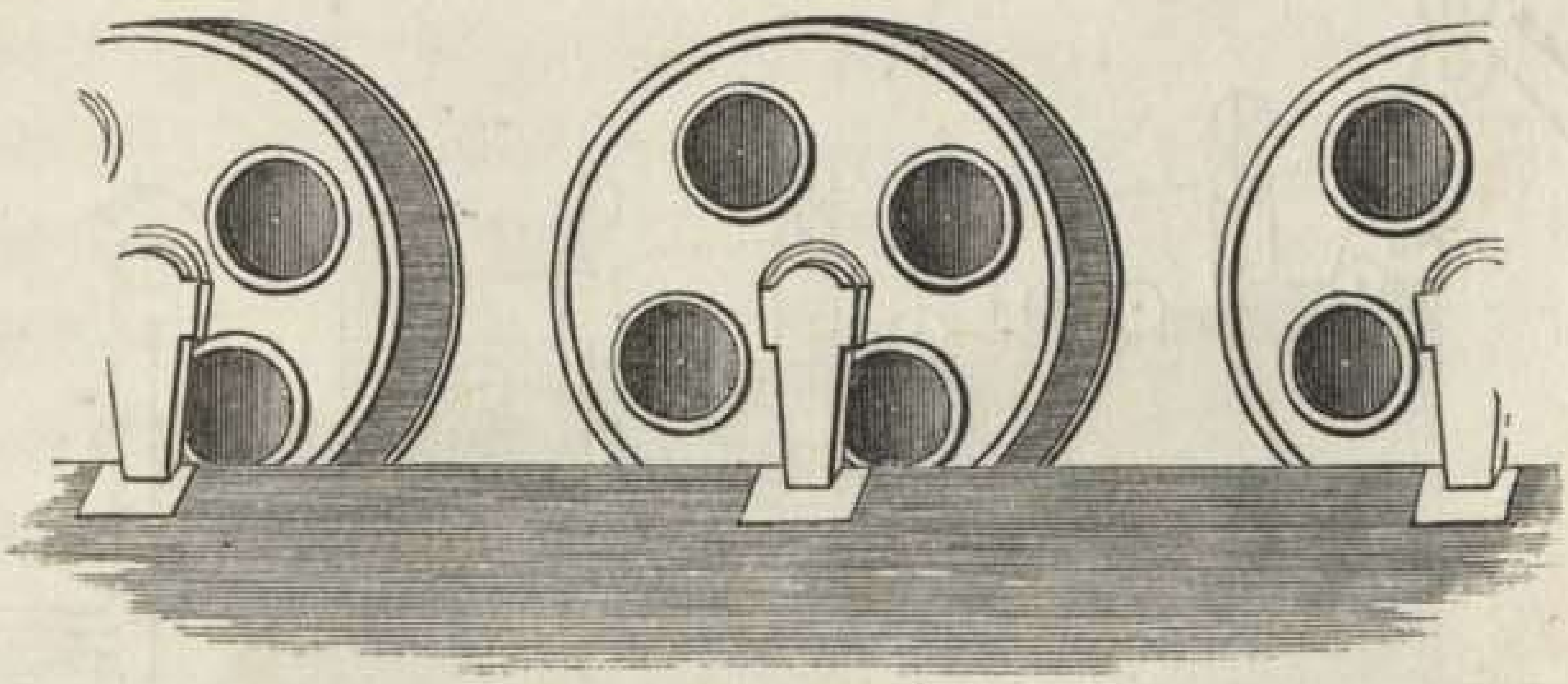
In general, the vegetable and animal fibres become coloured much more readily when unspun than when wove into cloth. Wool in flocks, after having been washed, digested in an alkaline ley, and bleached by sulphurous acid, takes more colour than when spun into yarn, and the yarn more than when wove into cloth. This doubtless arises from the comparative difficulty with which the solution of the colouring matter obtains access to the internal fibres of the spun or woven tissue. The colour of the interior of a piece of thick woollen cloth dyed in the piece, is often less intense to the eye than the colour of the exterior. Certain disadvantages, however, sometimes attend the dyeing of wool in flocks and in thread: some colours, for instance, are susceptible of alteration in the subsequent manipulations in weaving; the texture of the fibre is sometimes altered so as to present inconveniences in these operations, and it is more expensive from the subsequent waste of some of the material.

The routine of finishing operations practised on cloths after being dyed, is varied considerably, according to the style of work and the nature of the stuff operated on. When the goods have remained a sufficient length of time in the dye-beck, they are removed and carefully washed in water to separate the coloured liquid retained mechanically between the fibres. The drying of the washed goods, if of silk and wool, is usually effected by exposure to the air at common temperatures; but occasionally heat is applied, the goods being introduced into a well ventilated apartment heated by the circulation of steam-pipes. The drying of goods dyed with delicate colours should always be performed in the shade.

The following account of the course of finishing operations practised on calico printed and dyed according to the madder style, will afford a general view of the treatment of cotton goods after having been dyed by means of a vegetable infusion with the intervention of a mordant. Some of the operations here noticed are unnecessary, however, in other styles of dyeing and printing.

Immediately contiguous to the dye-beck are usually placed two stone cisterns containing cold water, each surmounted by a reel, similar to that shewn in figs. 31 and 32. In one of these cisterns the cloth is washed as soon as it is taken out of the dyeing liquor, motion being communicated to the cloth by means of the reel. From the first cistern the pieces are transferred to the second, containing clean cold water, and from thence to a washing vessel of particular construction, called the *dash-wheel* (fig. 33).

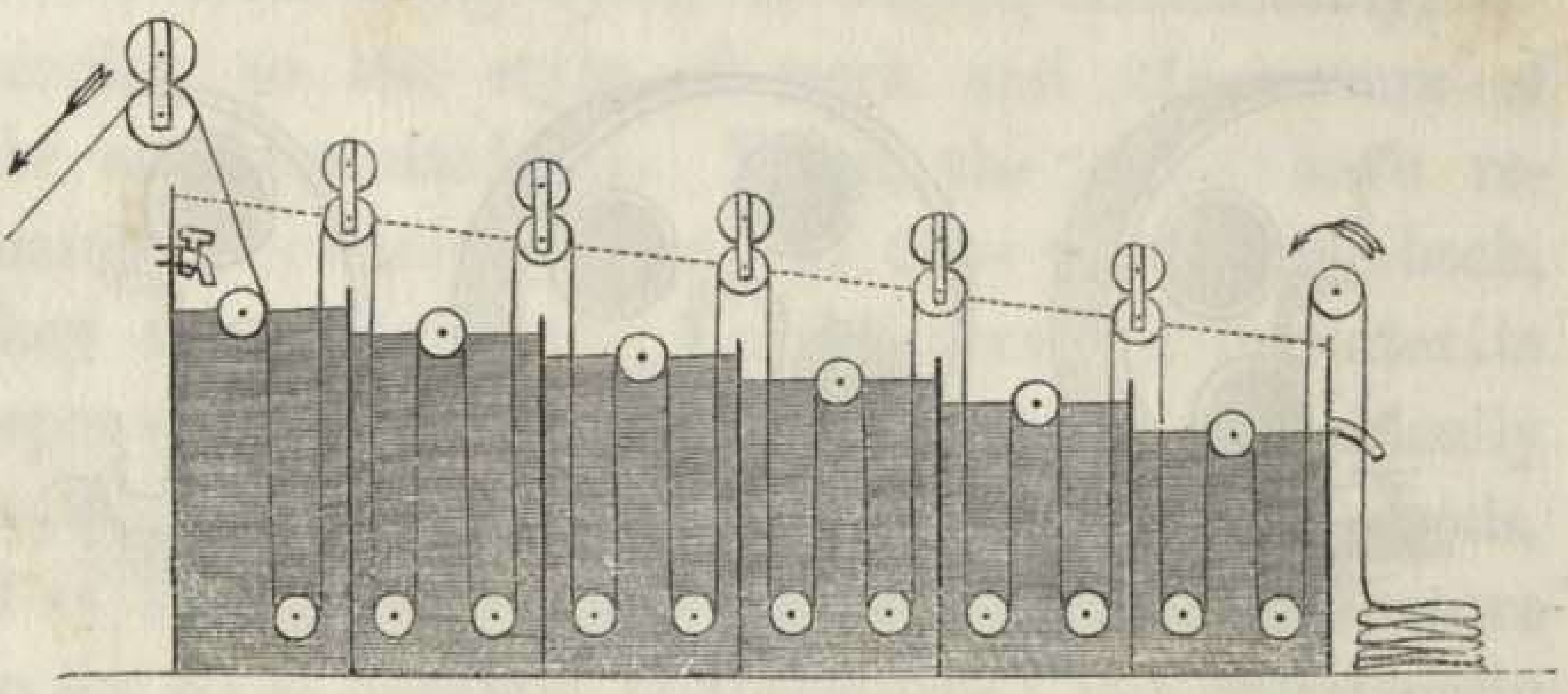
Fig. 33.



This is a hollow, circular, perpendicular wheel of five or six feet in diameter, and nearly two feet in depth, divided into four equal compartments by partitions proceeding from the axis to the circumference, each of which has a circular opening on one face of the wheel. Water is admitted into the compartments by a pipe concentric with the axis on which the wheel rotates. The pieces of cloth to be washed are put into the compartments through the circular openings in front, and water being admitted, the wheel is made to rotate rapidly, and thus wash the cloth with considerable agitation.

In the washing of cloths which require delicate treatment, as those dyed with fancy or spirit colours, for which the action of the dash-wheel is much too energetic, another washing apparatus is employed, called the *rinsing machine*, an idea of the ordinary construction of which will be afforded by the representation of its longitudinal section at fig. 34. It consists of a rectangular wooden cistern of from twenty to thirty feet long, three feet wide, and four feet high at one end, and three feet high at the other. The cistern is divided transversely into from six to

Fig. 24.



ten compartments, by partitions which gradually decrease in height from the higher to the lower end of the vessel. In each compartment except the highest are placed three rollers, to regulate the passage of the cloth through the cistern, two of the rollers being near the bottom and the other at the top. Above each partition are placed two more rollers nearly in contact; and those above the higher end of the cistern and the first partition are squeezing rollers subject to considerable pressure, and worked by machinery connected with one of the driving shafts of the factory. The pieces of cloth to be washed are introduced into the cistern at the lower end, and traverse each compartment successively, being drawn through by the traction of the squeezing rollers at the upper end. A stream of clear water is made to flow into the cistern at the higher end and out at the lower, while the cloth is passing in the opposite direction; by which arrangement the cloth is brought successively into contact with purer portions of water and is discharged at the top perfectly clean. In the machine represented in the above figure, the water flows from one compartment into another through apertures near the tops of the partitions, and not over the partitions. In another form of the rinsing machine, the water passes from one compartment into the next through apertures at the tops and bottoms of the partitions alternately. It is to be observed that this machine is used only for goods which require more delicate treatment than is compatible with the dash-wheel or the wince-pit.

While the cloth is in the dye-beck, a considerable quantity of colouring matter attaches itself to the surface of the cloth, not in chemical combination with the mordant, but too strongly attached to be easily removed by washing in clean water. To get rid of this superfluous colour, the cloth, after having been washed at the dash-wheel, is winced either in a mixture of bran * and boiling water, containing about

* In effecting the removal of this excess of colouring matter, the most active constituent of the bran seems to be the husky part. The feebly combined colouring principle dissolved by the hot water and the mucilaginous matters present, instead of being retained in solution, is precipitated on the husky surface, and thus prevented from again attaching itself to the cloth. Coarse bran is better adapted for this purpose than fine, and flour seems to be altogether useless. An interesting memoir by M. Kœchlin-Schouch, on the use of bran in this operation (termed "clearing"), is contained in the ninth volume of the *Bulletin de la Société Industrielle de Mulhausen.*

a bushel and a half of wheat bran for every ten pieces of calico, or else in a dilute solution of soap. The addition of a little caustic alkali to the soap or bran is sometimes made; but neither an alkali nor soap can be used for this purpose without great care, as the tints of all vegetable colouring principles are slightly deteriorated by these agents. For most vegetable colouring matters besides madder, bran only is admissible; and even in bran-water, the wincing sometimes must not exceed a few minutes. With madder colours only, the wincing may be continued for from ten to twenty minutes.

The complete removal of the superfluous colour from a piece of cloth which is to present a white pattern is generally effected, when madder is the only vegetable colouring matter present, by wincing the cloth for a few minutes in a solution of chloride of lime, not stronger than 3° Twaddell (1015). This operation usually follows that of branning or soaping, but sometimes the branning is altogether omitted when the solution of chloride of lime is employed.

Few vegetable colouring matters, however, can be exposed to the action of chloride of lime without considerable deterioration; hence, when other dye-stuffs than madder are employed, the "clearing" of the dyed cloth is effected, sometimes by exposure to air and light, but the process of branning or soaping is generally found to be sufficient of itself.

After having been thus cleared of the redundant colour, the cloth is washed, and then submitted to an operation for expelling almost the whole of the water it contains; which consists either in passing it between two rollers revolving against each other under considerable pressure (squeezing rollers), or else in rotating the cloth so rapidly as to cause the water to be driven out by the centrifugal force thus excited. One of the machines used for the latter purpose is represented in perpendicular section across the centre at fig. 35, and as viewed from above in fig. 36: *a* and *b* are two copper cylinders connected together at bottom so as to form one vessel, which rotates with the axis *c*. These cylinders are enclosed in a wooden case *d*, which is in communication,

Fig. 35.

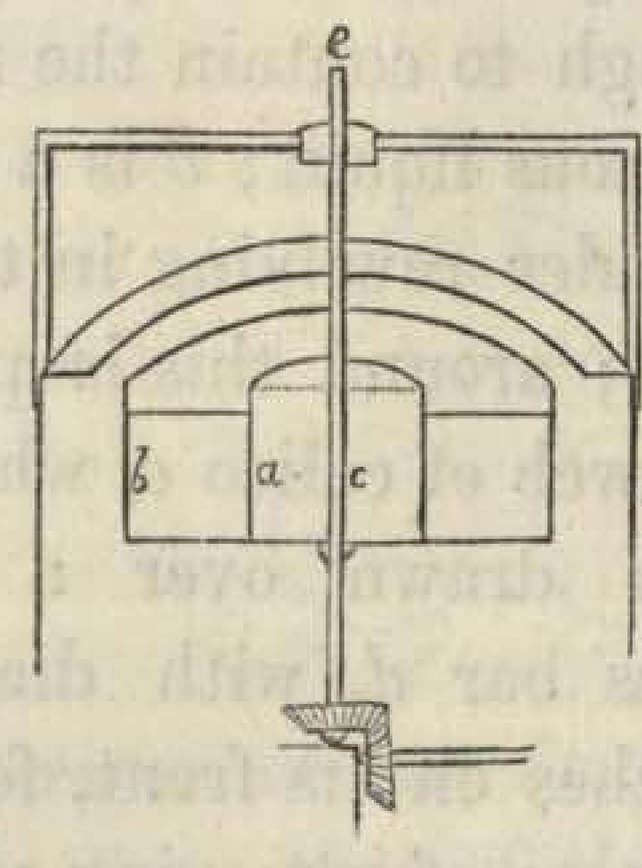
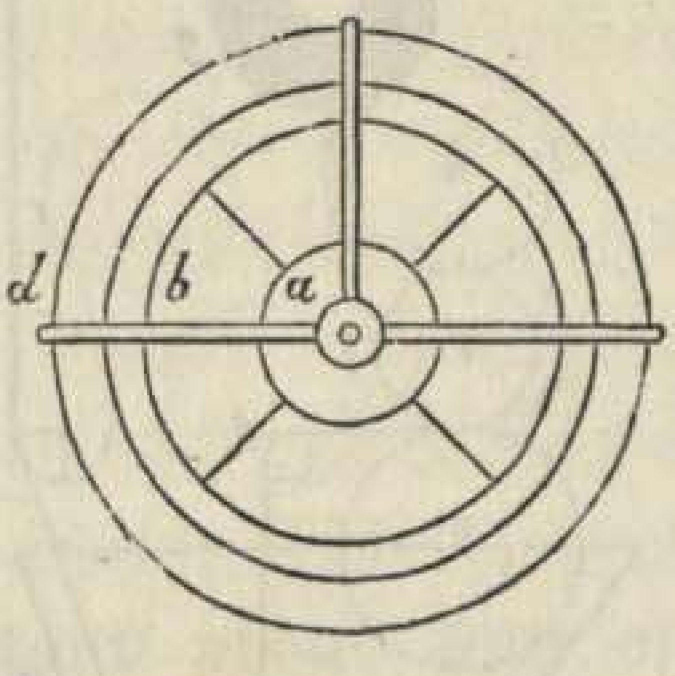


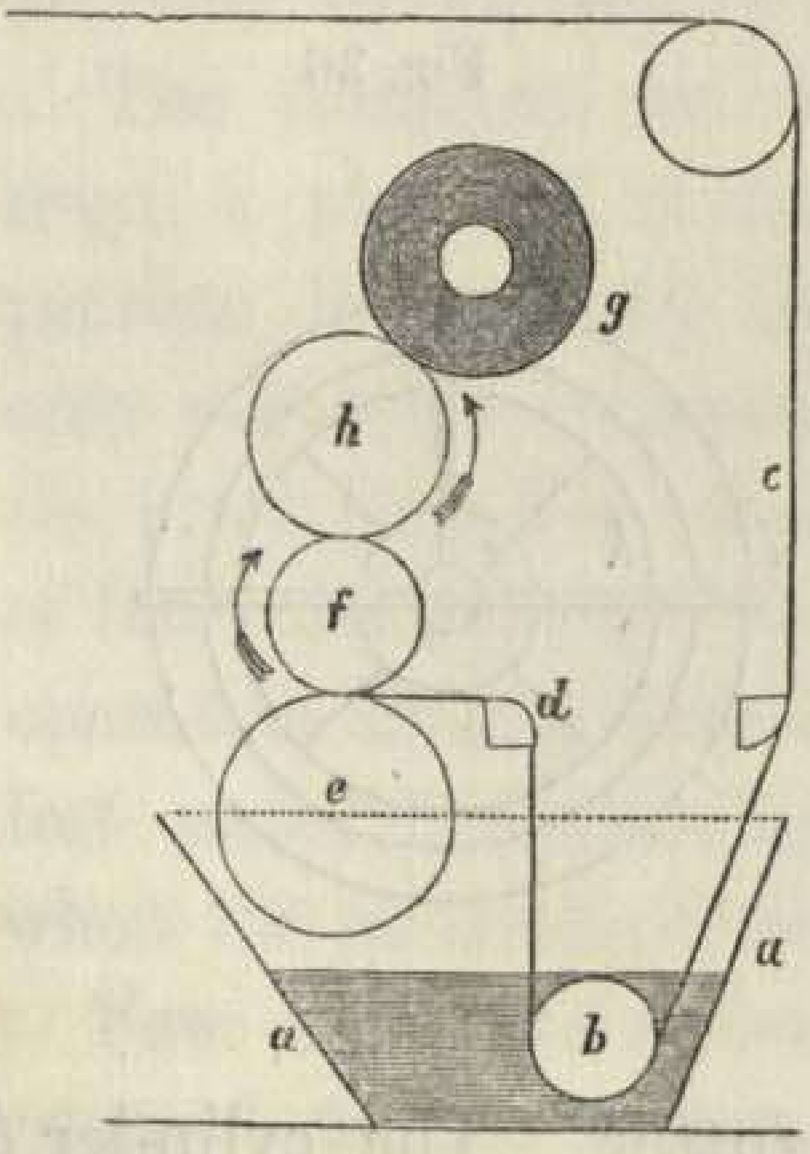
Fig. 36.



at bottom, with a drain or gutter. The cylinder *b* has a great number of small perforations, and is divided by partitions into four equal compartments. The wet cloth which is to be dried is placed in the compartments between the two cylinders, and the apparatus is rotated with a velocity of nine hundred or a thousand revolutions per minute; the water is thereby driven from the cloth through the perforations in the cylinder *b* to the outer case, from whence it flows out by a gutter or drain. After a few minutes the cloth becomes nearly dry, and when the machine is opened, is found to be strongly compressed against the perforated cylinder.* In another form of this machine, which works with much less noise than the preceding, the cylinders are arranged vertically, so as to form an apparatus somewhat resembling the dash-wheel (fig. 33, page 319).

When the cloth has been thus far dried, either by the squeezers or the "water extracter" just described, it is folded evenly and then passed, in a length of ten pieces, through a mixture of blue starch and water. A cross section of the *starching machine* is represented in fig. 37: *a* is a wooden trough to contain the mucilaginous liquid; *b* is a small cylinder revolving in the liquid; around this is passed the web of calico *c*, which is then drawn over a fixed brass bar *d*, with diagonal notches on its front, for the purpose of removing creases from the cloth; *e* is a wooden cylinder covered with cloth, revolving in close contact with the brass cylinder *f*; the calico is passed between these cylinders to be freed from the superfluous starch, and is then rolled off upon the cylinder *g*, the axis of which is not fixed, but so contrived as to recede gradually from the wooden cylinder as the roll of calico increases in diameter.

Fig. 37.

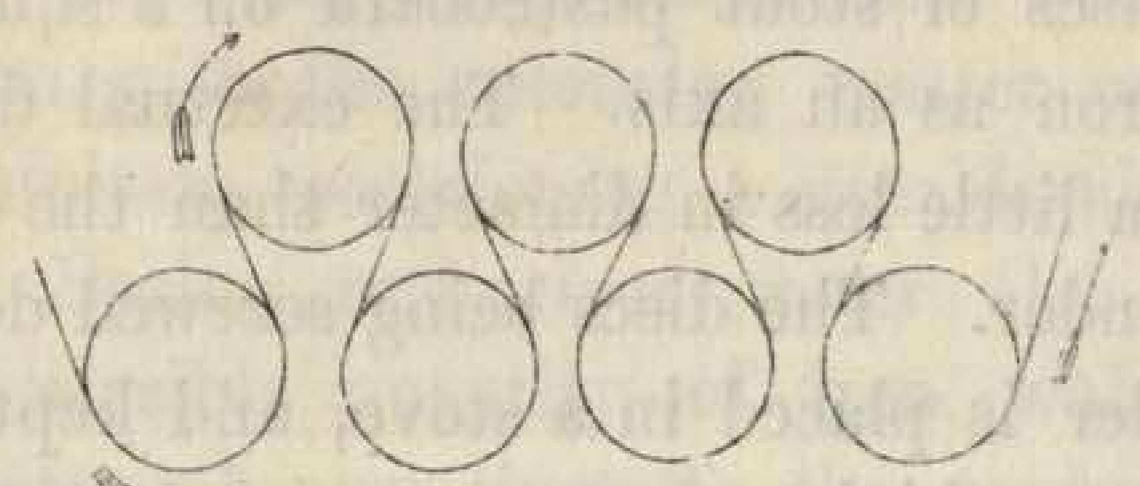


After being starched, the ten pieces of calico are

* This machine is known by the name of "water extracter."

passed through the *steam drying machine*, which consists of several hollow copper cylinders, each about twenty inches in diameter and three feet in length, fitted up with machinery by which all the cylinders or drums may be rotated together at the same velocity. Steam is admitted to the drums through stuffing boxes at one end of the axes, and at the other end are placed pipes to discharge the condensed water. The number of drums arranged together in one system varies from five to thirteen, according to the quantity of work required; they are sometimes placed in one line, but usually in two lines, one immediately over the other (as fig. 38), with the cir-

Fig. 38.



cumference of one drum distant about four or six inches from that of the next in the line of the axes of the drums. The calico passes through the machine in the direction of the arrows in the above figure. The drums are surmounted by a hood and flue for the purpose of conducting the steam out of the chamber.

The last finishing operation to which dyed and printed cottons are sometimes subjected, is *calendering* or glazing, the object of which is to make the surface of the cloth smooth, compact, and uniform. This is effected by passing the piece between two cylinders revolving in such close contact that their pressure gives the cloth the appearance of having been ironed. One of the cylinders is made of iron, and is hollow for the purpose of admitting steam or a hot iron rod, when the application of heat is necessary. The material of the other cylinder was formerly wood, but for some years past pasteboard has been very generally substituted. The cylinder of paper has several decided advantages over that of wood. It takes a finer polish, it has no tendency to crack or warp, and from having a certain degree of elasticity, it gives a more equal pressure on all parts of the cloth than could be applied by a wooden cylinder. The paper cylinder is constructed by placing circular discs of stout pasteboard on a square bar of wrought iron as an axis. The external discs are of cast iron, a little less in diameter than the remainder of the cylinder. The discs being screwed down tight, the cylinder is placed in a stove, and kept for several days at as high a temperature as the paper will bear without being charred or rendered very brittle. As the moisture is driven off, the pasteboard shrinks, and the screws must be tightened to keep the mass as compressed as possible. When no further diminution in bulk is perceived, the cylinder is removed from the stove, and carefully turned on a lathe. The diameter of the paper cylinder is usually fourteen inches, and that of the opposed iron cylinder eight inches. Four or five cylinders are commonly arranged together one over the other on the same frame.

The glazing of calicos was formerly executed by the hand with a hot iron, at an expense of about one shilling per piece of twenty-eight yards; the cost of glazing by machinery as above, is from threepence to sixpence per piece.

The purity of the water employed in dyeing operations is a subject which deserves the especial attention of the practical dyer. The finest colours are in almost all cases obtained by making use of distilled water, that being free from all earthy impurities. Rain water and the water of an Artesian well are, in general, better adapted for dyeing than spring water and river water, as the latter contain in solution a quantity of lime, which sometimes falls down in combination with the colouring matter as an insoluble precipitate, occasioning a considerable loss of dye-stuff. Spring and river water also generally contain a sensible quantity of iron, which always communicates a brown tinge to the goods washed in such waters.

When the yellowish Dutch madder is boiled with pure distilled or rain water, the residuary ligneous matter has a light brown colour, and imparts only a faint red colour to a boiling solution of alum. When, on the other hand, spring water is substituted, the residue is dark reddish-brown, and a solution of alum in which it is boiled becomes of a dark red colour. In the first case, the quantity of madder red remaining in the residue is much less than in the second. The madder red at first dissolved is precipitated by the lime of the spring water, imparting to the residue its dark colour, and is dissolved by the boiling solution of alum. Hence pure water dissolves more madder red than water holding lime in solution. Similar results are obtained with Fernambouc wood and logwood. (Dr. F. Runge, *Farben-chemie.*)

In some print-works in Lancashire distinguished for their fancy styles, it is a common practice to add a little dilute sulphuric acid to the water, if the latter contains carbonate of lime. The sulphuric acid converts the carbonate into sulphate of lime, which scarcely affects the brilliancy of the colours of the dyed or printed goods. It is of importance that there should be no excess of the acid. When cochineal colours are washed, distilled water is usually employed; but where this cannot be readily obtained in sufficient quantity, water treated with acid, as above, is used. These remarks are applicable to water containing calcareous matters only.

Dr. Clark's process for purifying water from carbonate of lime has not yet been introduced into the Lancashire print-works, but if efficiently conducted, it would no doubt be found highly advantageous.

Water which infiltrates marshy ground often contains in solution a quantity of decomposed vegetable matter, which is also very detrimental to certain colours. Not only is the shade of colour modified by the attachment of the organic matter, but certain metallic colouring materials, especially chrome-yellow and chrome-orange, are decomposed and converted into a brownish-black substance through the action of the organic matter. This proceeds from the generation of soluble earthy or alkaline sulphurets through the decomposition of the soluble sulphates which spring water always contains; the blackening of the chrome-yellow and chrome-orange is due to the formation of sulphuret of lead by the action of the soluble sulphuret thus produced.

A simple and efficacious method of rendering hard water well adapted for dyeing operations is practised at the Dukinfield branch of the Mayfield print-works, Manchester, on all the water consumed there, which amounts to six or eight hundred thousand gallons daily. It merely consists in mixing the refuse of the madder dye-becks with the water; the remaining colouring matters of the madder then precipitate the iron and lime in an insoluble form, and the water is obtained clear and fit for use by allowing the precipitate to settle in a large reservoir, and then filtering the water through a bed of gravel.

At an extensive silk-dyeing establishment in London, the only water employed is that raised from an Artesian well.

In one dyeing process, however, namely, the production of a black colour by means of infusion of galls, valonia, or sumach, and copperas, the water which is preferred by some dyers is hard spring water. To produce in a liquid a given depth of colour, distilled water requires more dye-stuff than common spring water. This is illustrated in the following experiment devised by Mr. Phillipps. Into two glass jars of the same size, each half filled with distilled water, introduce equal quantities of infusion or tincture of galls or sumach, and an equal number of drops (only three or four) of a solution of copperas. A faint purplish colour will be developed in both jars; but if one is filled with spring water, the colour in that rapidly becomes dark reddish-black, and one-half more water is required to reduce it to the same shade of colour as the other. The water which is found by experience to be best adapted for dyeing with galls and sulphate of iron differs from distilled water in containing sulphate of lime, carbonate of lime held in solution by free carbonic acid, and chloride of calcium. The beneficial ingredient seems to be the carbonate of lime, which possesses slight alkaline properties; for, if the smallest quantity of ammonia, or of bicarbonate of potash, is added to the distilled water in the above experiments, the purple colour is struck as rapidly and as deeply as in the spring water; chloride of calcium and sulphate of lime, on the contrary, produce no sensible change either in the depth of colour or the tint. The effect is no doubt referable to the action of the alkali or lime on the protosulphate of iron, by which the sulphuric acid of the latter is withdrawn, and hydrated protoxide of iron set free; for protoxide of iron is much more easily peroxidized and acted on by tannic and gallic acids (the dyeing principles of galls) when in the free and hydrated state, than when in combination with sulphuric acid. Neither the caustic fixed alkalies (potash and soda) nor their carbonates can be well introduced in the above experiments, as the slightest excess reacts on the purple colour, converting it into a reddish-brown. Ammonia, lime-water, and the alkaline bicarbonates also produce a reddening, and if applied in considerable quantity, a brownish tinge.

But the dyeing operations in which hard water is preferable to soft are so few in number, that the generality of the above statement concerning the superiority of soft water is scarcely at all affected.

§ IV. CALICO-PRINTING PROCESSES.

Although the different methods of procedure in the printing of cottons are almost as numerous as the different kinds of patterns which may be produced, yet each colour in a pattern is always applied by one of six different styles of work, by the proper combination of two or more of which the cloth may be ornamented with any pattern, however complicated. These styles are quite distinct from one another; each requires a peculiar process and a different manipulation.

The six styles alluded to are the following:

1. *Madder style, for soluble vegetable and animal colouring materials.* — In this kind of work, which derives its name from being chiefly practised with madder, the thickened mordant is first imprinted on the white cloth in patterns, and after the cloth has been aged and dunged, the colour is imparted by passing the cloth through the dye-beck. On those portions of the cloth on which the mordant is applied, the colouring matter attaches itself in a durable manner, but on the unmordanted portions the colour is feebly attached, so that it may be wholly removed by washing either in soap and water, in a mixture of bran and water, or in a dilute solution of chloride of lime.

2. *Topical style, for steam and topical colours.*

—Such colouring matters as are incompletely, or not at all, precipitated from their solutions on being mixed with certain solutions of a mordant, are sometimes printed on the cloth with the mordant, and the fixation of the colour is afterwards effected by exposing the cloth to steam. Some colouring matters applied topically in a state of solution become firmly attached to the cloth without a mordant and without the process of steaming, but merely by drying with exposure to the air.

3. *For mineral colours* (*padding style*).—To produce a figure in a mineral colouring material the cloth may be first printed with one of the two saline solutions, and be afterwards uniformly impregnated with the other. To obtain a ground of a mineral colour, one or both of the solutions may be applied by the padding machine.

4. *Resist style.*—In the processes referable to the resist style, the white cloth is first imprinted with a substance called the *resist*, or *resist paste*, which has the property of preventing those portions of the cloth on which it is applied from acquiring colour when afterwards exposed to a dyeing liquid. Resists are divisible into two classes; one is employed to prevent the attachment of a mordant, and the other that of a colouring matter.

5. *Discharge style.*—The object of the processes belonging to this style of work is the production of a white or coloured figure on a coloured ground. This is effected by applying topically to the cloth already dyed or mordanted, a substance called the *discharger*, which has the property of decomposing or dissolving out either the colouring matter or the

mordant. Chlorine and chromic acid are the common discharging agents for decomposing a vegetable or animal colouring matter, and an acid solution for dissolving a mordant.

6. *For China blue.* — This is a very peculiar style, and is practised with one colouring matter only, namely, indigo. This pigment is printed on the cloth in its insoluble state, and is dissolved and transferred to the interior of the fibre by the successive application of lime and copperas, with exposure to the air.

The topical application of the colouring matter, mordant, discharge, or resist, may be made by five different methods:

1. The simplest is by means of a wooden block, of from nine to twelve inches in length, and from four to seven inches in breadth, bearing the design in relief as an ordinary woodcut; or, when the design is complicated, and a very distinct impression is required, the figure is sometimes formed by the insertion of narrow slips of flattened copper wire, the interstices being filled with felt. The block is worked by the hand, and is made of sycamore, holly, or pear-tree wood, on a substratum of some commoner kind of wood. It is charged with colour or mordant by pressing it gently on a piece of superfine woollen cloth, called the sieve, which is kept uniformly covered with the thickened colouring matter or mordant by an attendant boy or girl, called the "tearer," (corrupted from the French word tireur,) who takes the colour up by a brush from a small pot and applies it evenly to the woollen cloth. This cloth is stretched

tight over a wooden drum, which floats in a tub full of old paste or thick mucilage to give it sufficient elasticity to allow every part of the raised device on the block to acquire a coating of colour. The calico being laid flat on a table covered with a blanket, the charged block is applied to its surface (the printer being guided where to apply the block by small pins at the corners) and struck gently to transfer the impression. The application of the block to the woollen cloth and the calico alternately is continued until the whole piece of calico is printed. By the ordinary method, a single block prints only a single colour; hence, if the design contain five or more colours, and all be printed by block, five or more blocks will be required, all equal in size with the raised parts in each corresponding with the depressed parts in all the others.

If the design, however, requires different colours to be applied in figures in straight and parallel stripes, all the stripes may be applied by one block at a single impression, and the block is also charged with the different colours by a single application to the surface of woollen cloth. The colours to be applied are contained in as many small tin troughs as there are colours, arranged in a line. A little of each colour is transferred from the troughs to the woollen cloth by a kind of wire brush consisting of wires fixed in a narrow piece of wood. The colour is distributed evenly in stripes over the surface of the sieve, by a wooden roller or rubber covered with fine woollen cloth. For the rainbow style, the colours are blended into one another at their edges by a brush or rubber drawn to and fro in a straight line.

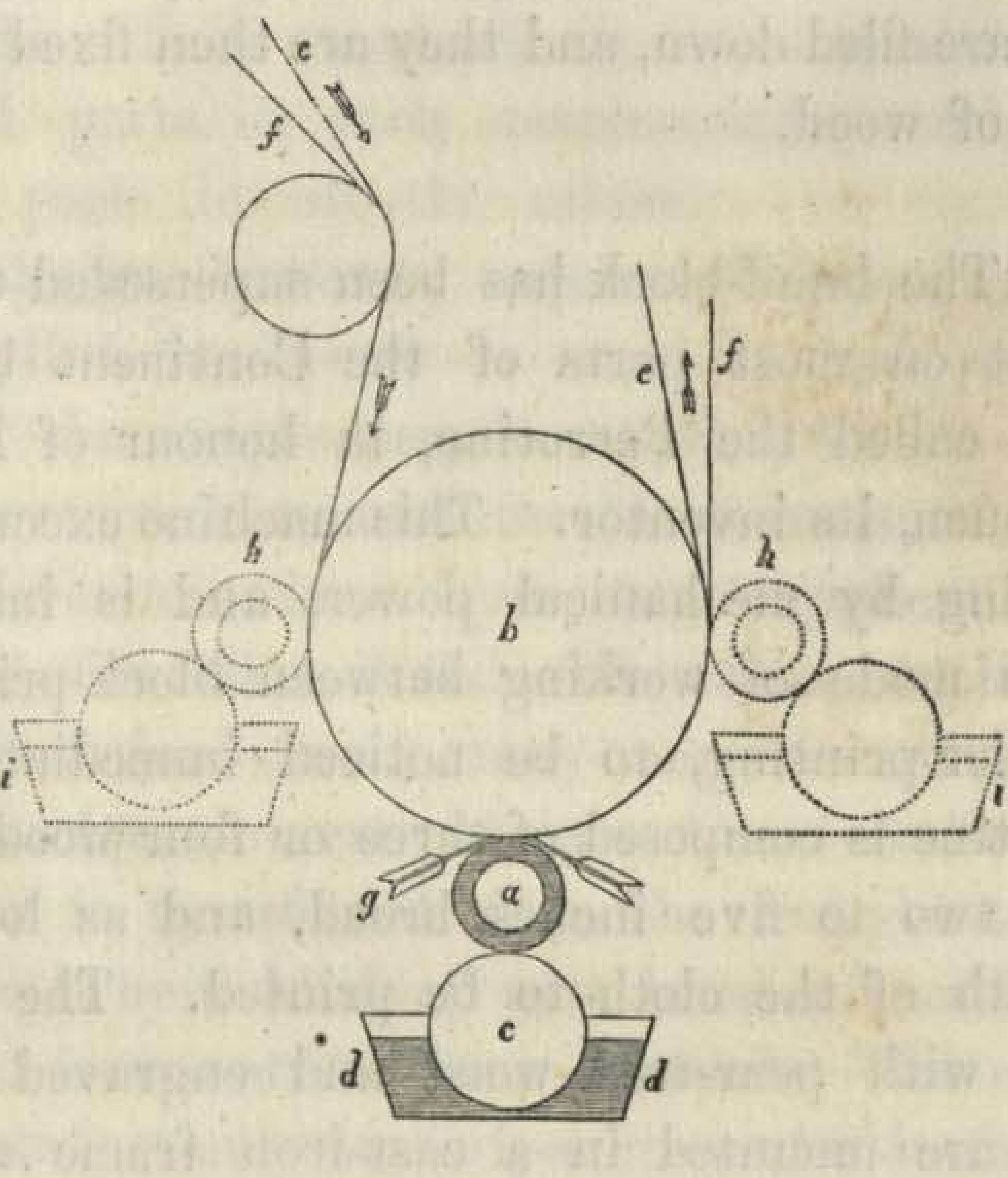
An important improvement in the construction of the hand-block has been recently adopted in most well conducted print-works, which consists in the application of a stereotype plate as the printing surface. To make the stereotype plate, a model is first formed from the pattern, about five or six inches in length, and from an inch and a half to five inches in width, according to the design. A mould is produced by stamping from the model; and from the mould, fixed in a block, stereotype copies are produced in a mixed metal, composed of eight parts of bismuth, five parts of lead, and three parts of tin. When a sufficient number of the pieces is prepared, their surfaces are filed down, and they are then fixed to a stout piece of wood.

2. The hand-block has been superseded to a great extent on most parts of the Continent by a machine called the Perrotine, in honour of M. Perrot, of Rouen, its inventor. This machine executes block-printing by mechanical power, and is intermediate in its mode of working between block-printing and cylinder-printing, to be noticed immediately. The perrotine is composed of three or four wooden blocks, from two to five inches broad, and as long as the breadth of the cloth to be printed. The blocks are faced with pear-tree wood and engraved in relief. They are mounted in a cast-iron frame with their planes at right angles to each other, and by a simple contrivance are charged with a coat of coloured paste and then pressed successively against the cloth to be printed. The cloth is drawn by a winding

cylinder between the engraved blocks and a square prism of iron, mounted so as to revolve on an axis against the blocks. Two or three only of these machines are in operation in this country.

3. About the commencement of the present century the hand-block and flat copper-plate, till then the only means of impression possessed by the printer, began to be superseded, for most styles of work, by cylinders of engraved copper. A general idea of the nature of this mode of printing may be conceived with the assistance of the annexed figure; *a* represents

Fig. 39.



sents the engraved cylinder or roller, mounted on a strong frame-work, so as to revolve against two other cylinders *b* and *c*. The cylinder *c*, which is covered with a woollen cloth, dips into the trough *d*, containing the solution of the colouring matter or mordant properly thickened, and thus acquiring itself a coating of the colour imparts some of it in the act of rotation to the engraved roller *a* : *b* is a large iron drum or cylinder, the surface of which is rendered elastic by several folds of woollen cloth; around this drum travels an endless web of blanket-stuff, *e*, in the direction of the arrows, accompanied by the calico passing between it and the engraved cylinder. The pressure of the cylinders against each other is regulated by screws or levers, which can be tightened or slackened at pleasure.

The excess of colouring matter or mordant which is communicated to the engraved roller by the cylinder *c* must obviously be removed before it comes into contact with the calico; this is accomplished by scraping the surface of the roller as it revolves, by a sharp-edged plate, usually of steel, called the *colour doctor* (*g*). Another similar plate is placed on the opposite side, called the *lint doctor*, the office of which is to remove the fibres which the roller acquires from the calico. With some colour mixtures and mordants, those containing salts of copper for instance, doctors composed of gun metal, bronze, brass, and similar alloys, are substituted for those of steel, as the latter would become corroded through the chemical action of the mordant or colour mixture.

Such is the method of printing calicos by the roller for a single colour; but the mordants or mixtures for two, three, or even eight colours may be applied at the same time by having as many engraved rollers with their appendages revolving simultaneously against the iron drum, as represented in fig. 39, by the dotted cylinders and troughs *h*, *h*, *i*, *i*. Extreme nicety of arrangement is required to bring all the rollers to print the cloth at the proper places, but when once properly adjusted each may be made to deposit its colour or mordant on the calico with the greatest certainty and regularity.

The diameter of the printing roller varies from four or six inches to a foot or even more; its length varies from thirty to forty inches, according to the breadth of the calico to be printed. It was formerly made of plates of copper hammered into a circular form and joined by brazing; but as the engraving easily gives way on the brazed joint, the roller is now bored and turned from a solid piece of metal. The engraving is not commonly etched by the ordinary graver, as was formerly done at a great expense, but by the pressure of a steel roller, called the *die*, from three to four inches in length (according to the pattern), containing the figures in relief which it imparts in intaglio to the softer copper. The steel die is made in a similar manner by powerful pressure against another steel roller called the *mill*, of similar size, which is engraved by the common graver while in the soft state, and afterwards hardened by being heated and then plunged into cold water. The steel die to receive the figure in relief is also in the soft state when pressed against the hardened engraved mill, and is itself hardened before being applied to the copper roller. The cost of engraving a roller in this manner is very little more than one-eighth that of engraving by the hand.

For some peculiar styles of pattern, the copper roller is etched instead of being engraved by indentation. The roller being heated by the transmission of steam through its axis, is covered with a thin coat of resist varnish, and when it is cold, the pattern is traced with a diamond point by a very complicated and ingenious system of machinery, the roller being slowly revolved at the same time in a horizontal line beneath the tracer. After having been etched on its whole surface, the roller is suspended for about five minutes in a trough containing dilute nitric acid, which dissolves the copper in the lines exposed by the removal of the varnish, but the parts still covered remain unacted on. The importance and value of this method arises from its affording an endless variety of curious configurations, which can hardly be copied or even imitated by the hand engraver.

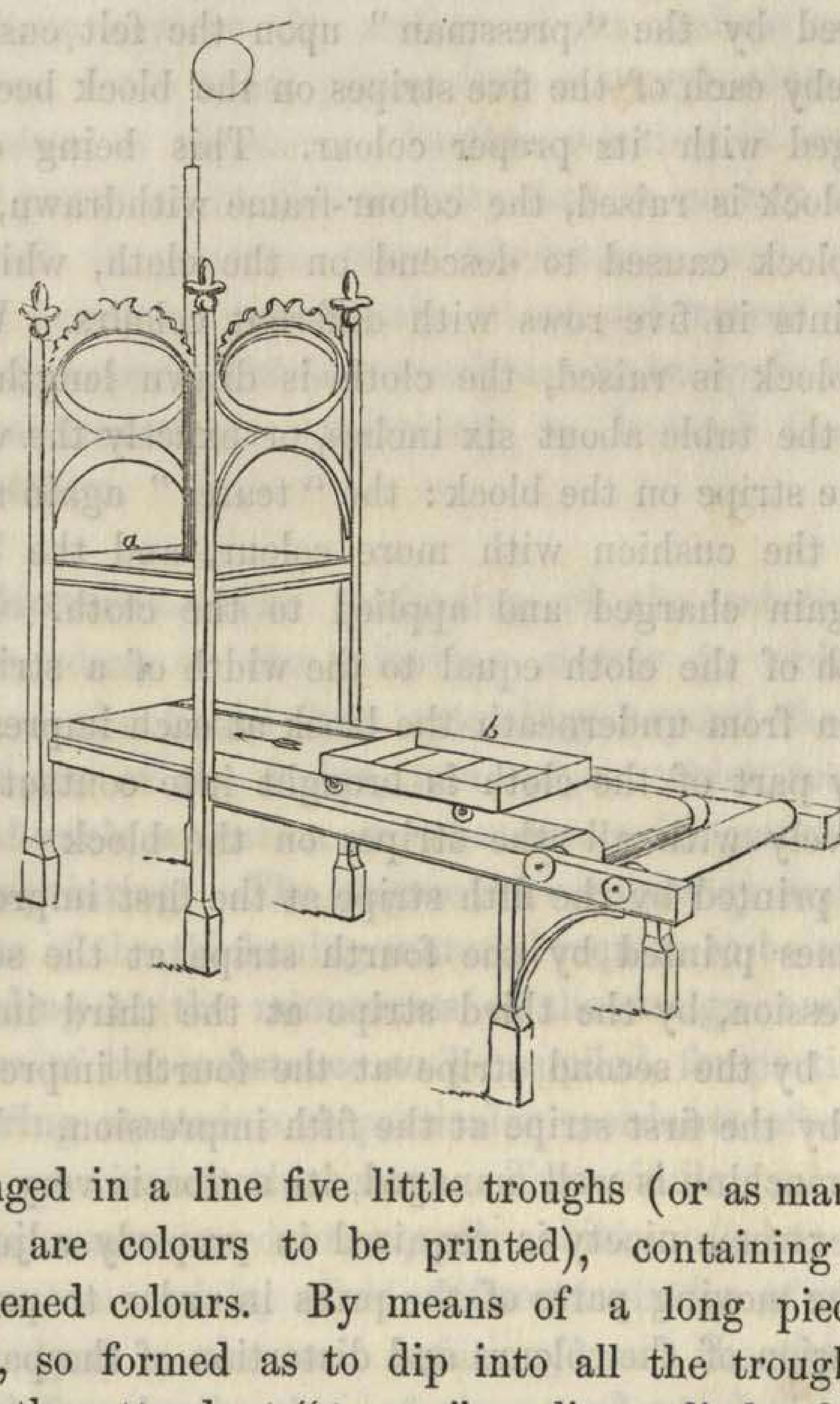
The following ingenious method of imparting a printing surface to a copper roller has been extensively practised of late in one of the best conducted print-works in Lancashire. It is only applicable to rollers to be used for printing a full ground, sprigs or other designs being left blank, for grounding in other colours if required by the block, at a subsequent operation.

The copper roller is, in the first place, painted with a resist varnish on its whole surface, with the exception of the figures to be left blank; and to render the blank parts perfectly clean, the roller is dipped, first, into weak nitric acid, and immediately afterwards, into clean water. From the water, the roller is transferred to a solution of sulphate of copper and placed in connection with a galvanic battery, whereby it acquires a coating of copper on the designs where the varnish had not been applied. These raised designs are afterwards polished smooth, so that when the roller is in use, they become perfectly cleared by the "doctor," and the ground only is imprinted on the cloth. It will be observed that this method of obtaining a printing surface is essentially different, in principle, from the etching process just described; in one method, the surface of the roller is covered with varnish on the parts to be raised, and in the other, on the parts to be depressed.

4. A very ingenious method of printing has been lately introduced, distinguished as "press printing," by which block printing with several different colours may be executed at one impression. A sketch of the principal parts of the press-printing machine is shewn in fig. 40. The block itself *a* consists of a well prepared tablet of wood, about two feet six inches square, supported in an iron frame in such a manner that it can be raised or lowered vertically at pleasure. The face of the block is divided into as many stripes (crossways with the table) as there are colours to be printed, which we may suppose, for illustration, to be five. The stripes are about six inches in breadth and as long as the breadth of the cloth to be printed; each one prints a different colour, and the whole five form together the combined pattern. The printing surfaces are stereotype casts, made of the mixed metal, bismuth, tin, and lead (see page 335).

The mode of applying the colours to the printing surface is very ingenious. At the bottom of the wooden frame *b*, near to one end of the table, is a felt cushion about the same size as the entire block, and immediately within one side of the frame are

Fig. 40.



arranged in a line five little troughs (or as many as there are colours to be printed), containing the thickened colours. By means of a long piece of wood, so formed as to dip into all the troughs at once, the attendant "tearer" applies a little of each of the five colours to the surface of felt, over which the colours are evenly spread by a brush in five stripes without any intermixture. The breadth of the stripes is the same as the breadth of the stereotype rows on the block.

The cushion being thus charged, the frame is slid forward on the table on a kind of railway, until it lies immediately underneath the block, which is then lowered by the "pressman" upon the felt cushion, whereby each of the five stripes on the block becomes charged with its proper colour. This being done, the block is raised, the colour-frame withdrawn, and the block caused to descend on the cloth, which it imprints in five rows with different colours. When the block is raised, the cloth is drawn lengthways over the table about six inches, or exactly the width of one stripe on the block: the "tearer" again slides over the cushion with more colour, and the block is again charged and applied to the cloth. As a length of the cloth equal to the width of a stripe is drawn from underneath the block at each impression, every part of the cloth is brought into contact successively with all the stripes on the block. The part printed by the fifth stripe at the first impression becomes printed by the fourth stripe at the second impression, by the third stripe at the third impression, by the second stripe at the fourth impression, and by the first stripe at the fifth impression. When this machine is well managed, its action is very neat; but extreme nicety is required in properly adjusting all the moving parts of the press in order to prevent confusion of the colours and distortion of the pattern.

5. The only mode of printing which remains to be noticed is "surface printing," which is merely a modification of roller printing, the cylinder being made

of wood instead of copper. The pattern is either cut in relief, as in the ordinary block, or it is formed by the insertion, edgeways, of flattened pieces of copper wire. This cylinder is mounted in a frame as the copper roller, and is supplied with colour by revolving against the surface of an endless web of woollen cloth, which passes into a trough containing the colour or mordant. Surface printing is scarcely at all practised in this country, but in certain styles of work it presents some advantages over copper roller printing, particularly where substances which corrode copper, but not wood, are to be applied. It is practised more extensively in Ireland than in Lancashire.

Thickeners.—The thickening of the solution of the mordant or the colouring matter in order to prevent the liquid from extending beyond the proper limits of the design, is a subject which requires considerable attention in the successful practice of calico-printing. The degree of consistency and the nature of the thickening material require to be varied according to the minuteness of the design and the nature of the substance to be applied, for particular colouring matters and particular mordants often require particular thickeners. Two similar solutions of the same mordant, equally thickened, but with different materials, afford different shades of colour when dyed in the same infusion;* and the time required for the fixation of the mordant during the

* Solutions of salts of iron or copper thickened with starch give a deeper colour to the cloth, when afterwards dyed, than the same solutions if thickened with gum arabic.

ageing is considerably affected by the nature and consistence of the thickening material with which the mordant had been applied.

The following is a list of the thickening materials commonly employed:

1. Wheat starch.
2. Flour.
3. Gum arabic.
4. British gum.
5. Calcined potatoe starch.
6. Gum senegal.
7. Gum tragacanth.
8. Salep.
9. Pipe-clay, mixed with either gum arabic or gum senegal.
10. China clay, mixed with gum arabic or senegal.
11. Dextrin.
12. Potatoe starch.
13. Rice starch.
14. Sago, common and torrefied.
15. Sulphate of lead, mixed with gum arabic or senegal.

The most useful thickeners are wheat starch and flour. When either of these or any kind of starch (not roasted) is employed, the mixture with the mordant or colouring matter requires to be boiled over a brisk fire for a few minutes in order to form a mucilage; the consistency of the mixture, when cold, diminishes if the ebullition is continued for a longer time. Neither flour nor any kind of unroasted starch is well adapted for thickening solutions containing a free acid or an acidulous salt; if other circumstances, however, should render the introduction of another thickener inadmissible in such a case, the acid or acid salt is always mixed with the thickening after the latter has been boiled and cooled to 120° or 130° Fahr. If the acid is boiled with the mucilage, the mixture completely loses its consistency.

Starch is almost the only thickener employed for mordants containing no free acid, and the mordant seems to combine with the stuff more readily when thickened with starch than when thickened with gum.

During the ebullition of starch with red liquor, a precipitate of subsulphate of alumina is produced (see page 283); but this precipitate is completely redissolved as the mixture cools, its solution being apparently facilitated by the starch.

Next to wheat starch and flour, the most generally useful thickener is gum arabic. With this substance, however, many metallic solutions, such as those of salts of tin, iron, and lead, cannot be well employed, as such solutions cause the formation of precipitates with an aqueous solution of gum. This objection to the use of gum does not apply to so great an extent to salts of copper.

The lime which is contained in all gum arabic met with in commerce is apt to affect the light shades of some colouring matters; but this inconvenience may be overcome by adding to the gum a small quantity of oxalic acid, which converts the lime into the insoluble oxalate.

Gum senegal is used for the same purpose as gum arabic.

British gum, torrefied or calcined farina, dextrin, and torrefied sago starch (known as "new gum substitute"), are intermediate, both in their properties and applications, between common starch and gum arabic. Calcined potatoe starch is chiefly used with solutions applied by the padding machine, which require very little thickening.

Gum tragacanth and salep are commonly employed as thickeners for solutions of salts of tin and for mixtures containing a considerable quantity of a free acid. Salep does not stiffen and harden the stuffs so much as most other thickeners, and is hence found advantageous for mixing with topical colours. It gives considerable consistence to water, but the mixture is apt to become thin on standing. It is remarkable that a mixture of solutions of gum tragacanth and gum senegal, both of the same strength, possesses only one-half or one-third the consistency of the two solutions before being mixed.

Pipe-clay, China clay, or sulphate of lead, when mixed with either gum arabic or gum senegal, is also used with acid mixtures, and with solutions of salts of copper when applied as resists for the indigo vat. The earthy basis acts as a mechanical impediment to the attachment of a colouring matter, when the latter is applied to the whole surface of the cloth.

When the mordant to be printed is colourless, or nearly so, as alum, red liquor, and salts of tin, it is mixed with a little decoction of logwood, Brazil wood, or some other fugitive dye, in order to render the design on the cloth more perceptible. This addition of colour is called *sightening*.

We proceed, in the next place, to consider some particular examples of printing processes in illustration of the six different styles of work noticed at page 331.

I. MADDER STYLE.

The madder style is applicable, not only to the dye-stuff from which it derives its name, but to nearly all organic colouring materials which are soluble in water, and capable of forming insoluble compounds with mordants, and is much more extensively practised than any other style.

The ordinary course of operations to which a piece of cotton is subjected in order to be printed and dyed according to this style is the following:

1. Printing on the thickened mordant, which is commonly done by the cylinder machine.

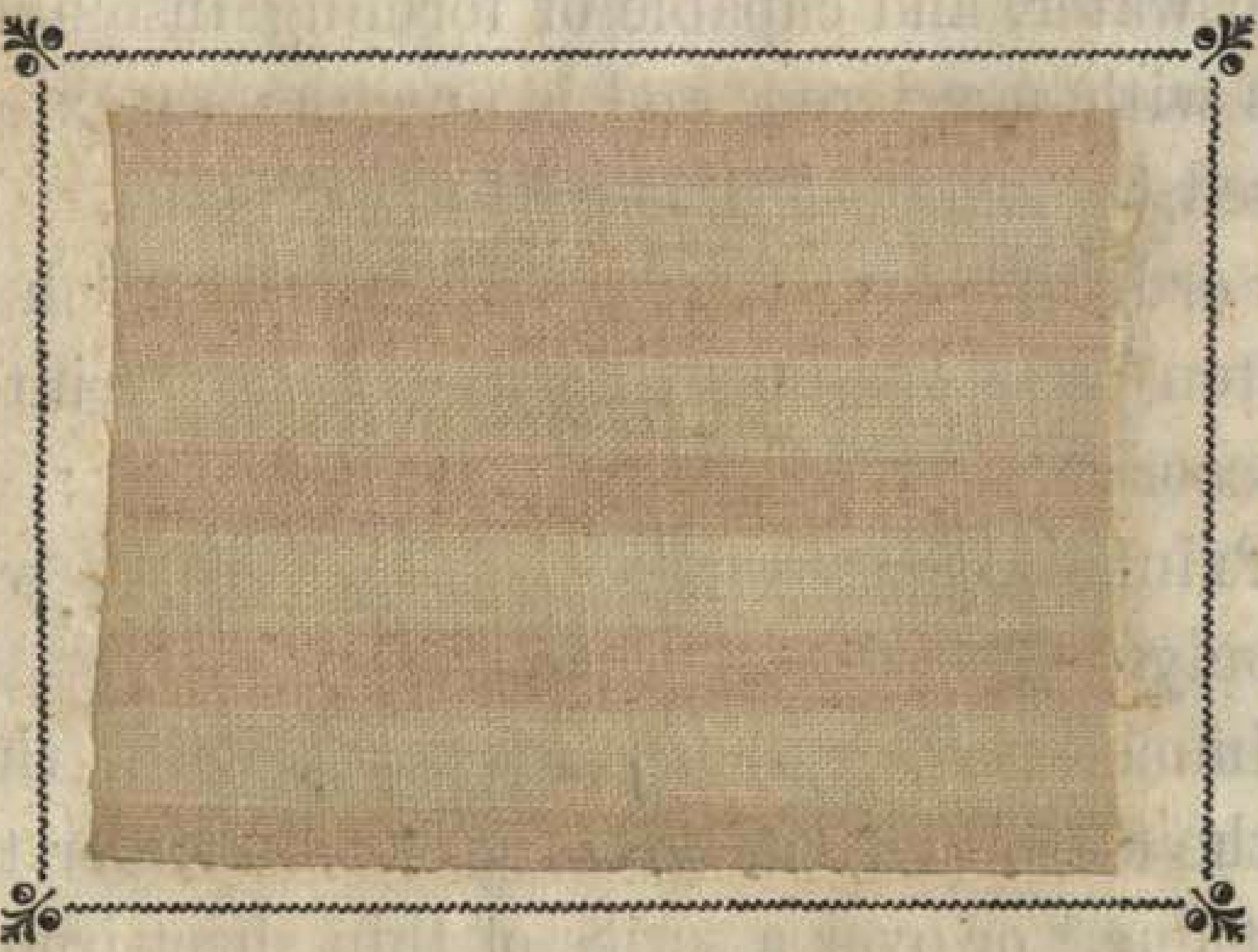
2. Immediately after the imprinting of the mordant, the cloth is dried by being drawn either through the hot-flue,* or over a series of thin sheet-iron boxes, heated by means of steam, and is then conducted into the "ageing" room, where it is suspended, free from folds, for one or two days, according to the nature of the mordant and the temperature. The ageing room should not be very dry, or heated above the ordinary temperature, except during winter.

During this suspension, the greater part of the mordant undergoes a chemical alteration, by which it becomes attached to the cloth in an insoluble state.

* The hot flue is a long gallery or passage, commonly heated by the flue of a furnace at one end, which runs through the whole length of the gallery on its floor. It is advantageous to have the upper surface of the flue formed of rough cast-iron plates, which become quickly heated and present a good radiating surface. A piece of calico (28 yards) is usually drawn through the flue in about two minutes.

Red liquor and acetate of iron part with a portion of their acetic acid; the former affords a deposit of subsulphate of alumina, the latter of subacetate of iron, as before explained; and the aluminate of potash affords a precipitate of alumina, through the action of the carbonic acid in the atmosphere (see page 285). Annexed is a specimen of calico in this

No. 1.



stage of the process, the mordant on which is red liquor, "sightened" with a little decoction of peach-wood or similar dye-stuff.

3. After having been suspended in the ageing room for a sufficient time, the printed cloth is drawn through the dung-becks, or else through a strong solution of dung substitute (page 307), whereby a part of the undecomposed mordant is separated from the cloth and prevented from acting on those parts which had not been printed, the thickening paste is removed, and the mordant remaining on the cloth becomes more strongly attached, by uniting with some of the constituents of the dung or of the substitute.

When taken out of the dung-becks, the cloth is immediately washed in a cistern of cold water, or sometimes both squeezed and washed, and then commonly winced for twenty or twenty-five minutes in a weak solution of substitute and size, by which the fixation of the mordant on the cloth is rendered complete. If the mordant is white, the cloth presents little trace of the design when taken from the substitute; the specimen No. 2. shews the appearance which

No. 2.

No. 1. acquires by being thus treated. (For an account of the manner of performing this operation, and of the probable action of the dung, see page 306.)

4. After having been well washed, the cloth is ready to be exposed to the dyeing liquor, in which it is kept for two or three hours, being constantly turned by a wince from one compartment of the dye-beck to the other. With madder and some other colours the goods are introduced into the cold mixture of water and ground dye-stuff, and heat is then gradually applied by the introduction of steam, until

the temperature of the liquid is very near ebullition (see page 313). When taken out of the dye-beck and simply washed in cold water, the cloth has the appearance of the specimen No. 3.

No. 3.

5. The next process to which the cloth is subjected is the "clearing," or the removal of the excess of colouring matter loosely attached to the exterior of the fibres. The processes for this purpose are varied with different dye-stuffs, and even with different varieties of the same kind of dye-stuff, according to their fixity (see page 321). With madder colours, where no sumach is employed, the goods may be cleared in the following manner, having been previously well washed at the dash-wheel:

1. Wince for half an hour in boiling bran-water;

2. Wince for half an hour or more in a dilute solution of chloride of soda or chloride of lime;

3. Boil the goods in soap-water containing half a pound of soap per piece;

4. Wince a second time in chloride of soda or lime, weaker than before;

5. Boil a second time in soap-water.

When the goods are dyed with Dutch madder and sumach,* soap cannot be well employed in the clearing process, but only bran and chloride of lime or chloride of soda, the latter being preferred. If dyed with the form of madder called *garancine* (see page 252), neither chloride of lime nor chloride of soda is admissible. Other precautions necessary to be attended to in the process of clearing and the finishing operations to which the calico is afterwards

No. 4.

subjected have been noticed in the preceding section. The specimen, No. 4, is the finished cloth.

The strength of the mordant, solution of dung substitute, dye-beck, &c., and the details of the process generally, vary considerably for the same colour-

* The tints of cloth dyed in the madder-beck are considerably heightened by the addition of a small quantity of sumach. One pound of sumach with eighteen or twenty pounds of Dutch madder will dye as much stuff as twenty-four pounds of madder without sumach. The addition of astringent substances to logwood, peachwood, and cochineal, produces a similar result.

ing matter and mordant, according to the quantity or fulness of the figure, and the depth of its colour. To impart such a stripe as that in the preceding specimen, the bleached cloth may be submitted to the following operations:

1. Printing on mordant of red liquor (of spec. grav. 1·042, thickened with a pound and a half of flour to the gallon), and drying by being drawn over steam boxes;

2. Ageing for three days;

3. Dunging, 1°, in a mixture of four gallons of dung and three hundred of hot water; and 2°, in a mixture of two gallons of dung and three hundred of hot water;

4. Wincing in cold water;

5. Washing at the dash-wheel;

6. Wincing for twenty minutes in a solution of dung substitute and size, made of two quarts of substitute liquor (page 309), one quart of cleansing liquor (page 308), and three hundred gallons of water.

7. Wincing in cold water;

8. Dyeing in the madder-beck, containing about two pounds of madder per piece of twenty-eight yards;

9. Wincing in cold water;

10. Washing at the dash-wheel;

11. Wincing in soap-water, to which some perchloride or nitromuriate of tin has been added;

12. Washing at dash-wheel;

13. Wincing a second time in soap-water;

14. Wincing in a solution of bleaching powder of spec. grav. 1015 (3° Twad.)

15. Washing at the dash-wheel;
16. Drying by the "water extractor" (page 323);
17. Folding;
18. Starching (page 324);
19. Passing through the steam-drying machine (page 325).

As the quantity of colouring matter which is deposited on the cloth in the dye-beck is much more dependent on the quantity of fixed mordant on the cloth, than on the strength of the dyeing liquid, a pattern comprising two or more different shades of the same kind of colour may be obtained by the same dye-beck, the cloth having been previously printed with the same kind of mordant at different strengths.

The pattern annexed (No. 5) is produced by the

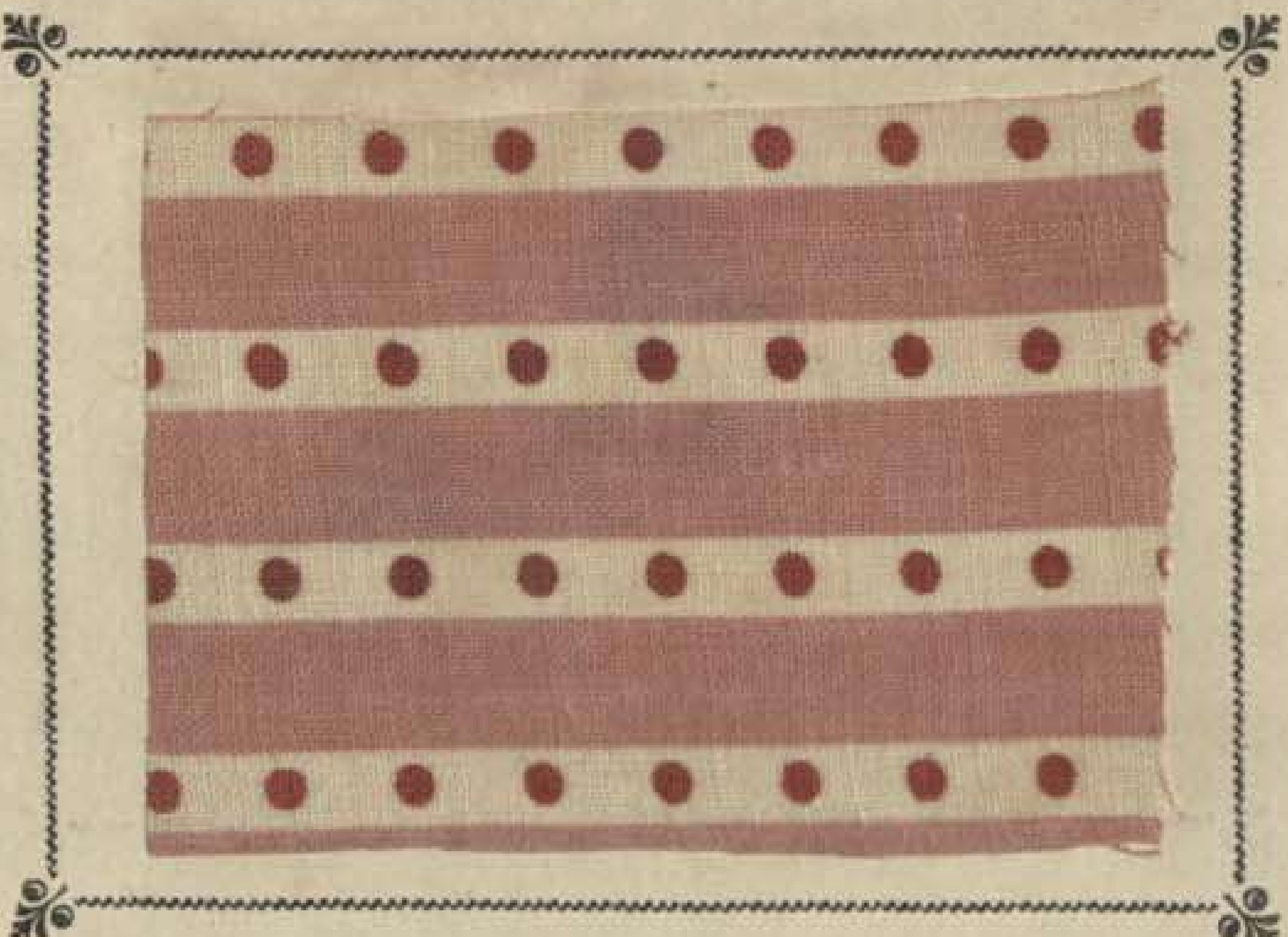
No. 5.

iron liquor mordant (pyrolignite of iron) at two different strengths, with the same infusion of madder. The mordant for the lilac is iron liquor of spec.

grav. about 1·010, thickened with three pounds and a half of British gum to the gallon. The mordant for the dark purple or black is iron liquor of spec. grav. about 1·020, thickened with a pound and a half of flour to the gallon. The two mordants may be printed on at once by the two-colour machine. The finest madder purples are obtained by a mixture of iron liquor with from five to six measures of "patent purple liquor," or "assistant mordant" (see page 294), thickened with British gum.

To produce different shades of red on the same piece from the same madder-beck, the cloth may be printed with red liquor of any density between 3° and 25° Twaddell. The thickener usually employed for red liquor is either flour, starch, or a mixture of equal parts of flour and starch. The proportion of the thickening ingredient is varied according to the

No. 6.



density of the mordant and the fulness or delicacy of the design; on the average, a pound and a half may be taken for a gallon of liquid. For a weak liquor and for a delicate figure, either British gum or gum arabic is substituted for starch or flour.

The mordants printed on the cloth for the specimen No. 6 were red liquor of spec. grav. 1·105 for the dark red spots, and the same liquid of spec. grav. 1·021 for the light red figure. Both solutions were thickened with four pounds of British gum to the gallon.

British gum is the best thickener for a solution of aluminate of potash.

As different mordants form compounds of very different colours with the same dye-stuff, a variety of colours may be communicated to the calico from the same infusion of colouring matter, provided as many kinds of mordants, or mixtures of mordants, had been previously applied. The annexed pattern

No. 7.

(No. 7), containing a design in black, purple, and two shades of red, was obtained by dyeing the cloth at one operation after it had been printed by the four-colour machine with the following mordants: iron liquor of spec. grav. 1·020 for the black; iron liquor of spec. grav. 1·012 for the purple; red liquor of spec. grav. 1·042 for the dark red; and red liquor of spec. grav. 1·010 for the pale red. The iron liquor for the black was thickened with a pound and a half of flour to the gallon. The weaker iron liquor for the purple and the two red liquors were thickened with three pounds of British gum to the gallon. After being printed, the cloth was "aged" three days, dunged, dyed with madder, soaped, and cleared in the ordinary manner.

To obtain on the same cloth the finest madder reds, purple, and black, it is sometimes better first to print on only the aluminous mordants for the reds, by the two or three-colour machine, and then to age, dung, and madder. The strong iron liquor for black, and the weaker iron liquor for purple, may be next grounded in their proper places by hand-blocks, after which the drying, dunging, and maddering are repeated. Sometimes the mordants are printed on at different operations, but the dyeing is performed in one beck. For example, the mordant for black is printed on first by the single-colour machine, after which the cloth is aged for a day or two; the mordants for the other colours are then grounded in by the hand-blocks, and the ageing, dunging, dyeing, &c., are performed in the usual manner. An endless variety of tints, from red to chocolate, may be obtained from the same madder-beck by mixtures of the iron and aluminous mordant in different proportions.

Quercitron is a dyeing material well adapted for the madder style of work. With a mordant of red liquor of spec. grav. 8° or 12° Twaddell, thickened with starch, it affords a bright yellow; with iron liquor of spec. grav. 2° or 3° Twad., thickened with starch, an olive-grey colour; and with a mixture of the iron and aluminous mordants, a great variety of yellowish-olive tints. To produce a yellow ground with quercitron, the cloth may be padded in red liquor of 10° Twad., and after being dried, aged for two days, and winced in warm chalky water, be dyed in an infusion of quercitron (made of from two to three pounds per piece), containing some glue or size. To get a yellowish-olive figure from the same infusion, the cloth may be printed with a mixture of red liquor at 11°, and iron liquor at 5° Twad., in equal measures, and then dried, aged, dunged, winced in chalky water, and dyed.

A very good orange is sometimes communicated to cotton goods in this style of work by dyeing in a mixed infusion of madder and quercitron, an aluminous mordant having been previously applied to the cloth. For a ground, the cloth may be padded in red liquor of 10° or 12° Twad., then winced in warm chalky water, and dyed in a decoction of two pounds of quercitron and a pound and a half of madder per piece. By varying the proportions of the madder and quercitron various shades of orange (from golden-yellow to scarlet) may be produced.

An endless variety of cinnamon, olive, and fawn coloured tints may be obtained by applying to the cloth mixtures, in various proportions of red liquor and iron liquor, and by dyeing the cloth in a mixed infusion of madder and quercitron. It is advisable not to have the temperature of the dyeing liquid above 140° or 150° Fahr.

Patterns in black and various shades of violet and purple may be imparted to cotton cloth, in the madder style, by means of a decoction of logwood as the dye-stuff, with iron liquor and red liquor as the mordants. To produce a black ground, the cloth may be padded in a mixture of equal measures of red liquor at 8° Twad., and iron liquor at 6° Twad.; and after having been dried, aged, and winced in chalky water, it may be dyed in a decoction of logwood made from two pounds and a half or three pounds per piece, with the addition of a small quantity of sumach. A grey colour is obtained in the same way by using very weak iron liquor and a weak decoction of the colouring matter; and a violet colour, by applying weak red liquor to the cloth.

Cochineal is another dye-stuff, the colouring matter of which is capable of being imparted to cloth by the madder style. It is chiefly applied in this way as a ground on which figures are afterwards produced by other styles. To obtain an amaranth-coloured ground, the cloth is padded in red liquor of spec. grav. from 11° to 13° Twad., and after being dried, aged, and winced in chalky water, it is dyed in a mixed decoction of cochineal, galls, and bran. A beautiful orange is obtained by a mixture of decoction of cochineal and decoction of quercitron, with an aluminous mordant; and fine lilacs and violets by decoctions of logwood and of cochineal, with the same mordant.

The madder style admits of the application to cloth of the colouring matters of several dye-stuffs besides those which have been alluded to. By combining two or more in the same dyeing liquid, and by varying the mordants, an endless variety of tints may be obtained; but a detailed account of such processes could not be included in the limited plan of the present article.

II. TOPICAL AND STEAM COLOURS.

The mere mechanical part of the process is simpler in this than in any other style of calico-printing. The thickened solution of the colouring matter is applied topically (mixed with the mordant when any is required), in a state fit to penetrate to the interior of the fibre, and after the cloth is dried, the colouring matter is fixed, either by exposure to the air or a precipitating agent, or by the action of steam. The operations of dunging, dyeing, and clearing are here altogether omitted.

The vegetable colours which may be applied to cotton by this style of work are chiefly those which are not at all, or incompletely, precipitated from their solutions when mixed with a mordant; the deposition of the insoluble compound of mordant and colouring matter is usually determined in such cases by the surface attraction of the tissue, frequently assisted by the application of heat. Not many colours applied in this way are remarkable for their permanency. A few topical colours are printed on the cloth in an insoluble state, as pigments, and remain attached principally through the starch or gum used as thickening.

The topical colours most extensively used in printing cottons are the following:

Black.—A very good topical black, known as "chemic black," may be imparted to cotton by means of a mixture of decoction of logwood, copperas, and pernitrate of iron, in the proportions of either of the recipes following:

No. 1.

1 gallon of logwood liquor (decoction of logwood) of spec. grav. from 6° Tw. to 8° Tw.,
4 ounces of copperas,
$\frac{1}{8}$ to $\frac{1}{12}$ gal. (according to the strength of the logwood liquor) of solution of pernitrate of iron of spec. grav. 50° Tw.
Thicken with either flour or starch.

No. 2.

1 gal. of logwood liquor at 8° Tw.,
2 ounces of copperas,
1 pint of solution of pernitrate of iron of 8° Tw.,
1$\frac{1}{4}$lbs. of starch.

The logwood liquor, copperas, and starch are boiled together for a few minutes, and when the mixture is cooled to about blood-heat the nitrate of iron is added.

This mixture may be printed on the white calico by the roller at the same time as the mordants for colours to be afterwards applied by the madder style.

After ageing for two days the black colour becomes so permanently attached to the cloth that it is very little affected by the remaining operations of dunging, washing, dyeing, and clearing.

Brown.—A very fast topical brown, forming the ground in the annexed specimen (No. 8), may be

No. 8.

communicated to cotton goods by a solution of catechu, mixed with a salt of copper and muriate of ammonia. The following proportions have been recommended to me by an eminent Lancashire printer:

1½ pounds of catechu,
¾ to 1 gill of solution of nitrate of copper of 90° Tw.,
6 to 8 ounces of muriate of ammonia,
1 gallon of water.
Thicken with either gum senegal or British gum.

Some printers are in the habit of using a mixture containing much less muriate of ammonia and more nitrate of copper than the above, such as the following:

$1\frac{1}{2}$ pounds of catechu,
3 ounces of muriate of ammonia,
2 quarts of water,
1 quart of pyroligneous acid of 2° Tw.,
3 pounds of gum senegal, and about
$\frac{1}{2}$ pint of solution of nitrate of copper of 100° Tw.

The catechu and muriate of ammonia are first mixed with the water and pyroligneous acid; the mixture is then heated and kept at the boiling point for ten minutes, after which it is allowed to settle for half an hour. The clear supernatant liquid is then decanted from the insoluble matters and mixed with the gum senegal, and when the latter is dissolved the solution of nitrate of copper is added.

The first of the preceding preparations probably deserves a preference. Both of them, like the above topical black, may be printed on the cloth by the compound machine, with mordants for colours to be applied by the madder style. During the ageing of the goods, the astringent principle of the catechu becomes fixed on the cloth in an insoluble state, but it is usual to complete the fixation of the colouring matter by passing the cloth through a solution of bichromate of potash previous to being dyed in the madder-beck. The specimen No. 8 is an example of a design in madder colours on the catechu ground; the manner of producing such a pattern will be again adverted to, as a part of the process is referable to the resist style of work.

The chemical change which takes place during the fixation of the astringent principle of the catechu is the absorption of oxygen. Catechu, or its colouring principle, exists in two forms; deoxidized and soluble in water, and oxidized and insoluble in pure water, but soluble in an aqueous solution of the deoxidized catechu. The form in which catechu is applied to cloth in the above mixtures is as a solution of the oxidized in that of the deoxidized catechu; and the chloride of copper, formed by the reaction of muriate of ammonia on nitrate of copper, acts as a slow oxidizing agent (through the decomposition of water) to the deoxidized catechu.

Spirit purple.—For a spirit or fancy* purple, such as that in the following specimen (No. 9), a decoction of logwood, mixed with a tin or an aluminous

No. 9.

mordant, is commonly employed. A gallon of logwood liquor of 6° Tw. may be boiled for a few minutes with a pound of starch, and when the mixture is lukewarm, there are added, first, a pint and quarter of solution of perchloride (nitromuriate) of tin at 120° Tw., and afterwards, a quarter of a pint of oil.

* All fugitive topical colours not fixed by steaming are termed spirit, fancy, or wash-off colours.

This mixture should be carefully stirred before being applied to the cloth. Some printers use a little less tin than is prescribed above, and add a very small quantity of pernitrate of iron.

After being printed with this mixture, the cloth should be suspended in a warm room for two days and two nights, and then washed at the rinsing machine.

Spirit chocolate.—A fancy chocolate or puce colour may be imparted to cotton by means of a mixture of logwood liquor, peachwood liquor, perchloride of tin, and a little nitrate of copper, thickened with either starch or British gum.

A much faster colour may be obtained by first printing on a mixture of logwood liquor, red liquor, and oxalic acid, and after ageing, passing the cloth through a solution of bichromate of potash. If the materials are employed sufficiently strong, an excellent black may be imparted by such a process. The black or chocolate-coloured substance thus produced is a compound of oxide of chromium with the colouring matter of logwood.

Spirit pink.—The following receipt for a topical pink has been recommended to me by a Lancashire printer:

1 gallon of peachwood liquor at 8° Tw.,
$1\frac{1}{4}$ pounds of starch,
$\frac{1}{2}$ gill of solution of nitrate of copper at 100° Tw.,
3 gills of solution of perchloride of tin,
4 ounces of "pink salt" (see page 289), and
1 gill of oil.

The peachwood liquor is first boiled briskly with the starch; the nitrate of copper is next added; and when the mixture is cooled to about blood-heat, the remaining ingredients are introduced.

Spirit yellow.—A fancy yellow, pretty much employed for grounding in by the block, is a mixture of decoction of French berries, red liquor, and oxalic acid, thickened with starch or gum tragacanth. Some printers use, instead of red liquor and oxalic acid, a mixture of perchloride of tin and alum, and thicken with starch; others, perchloride of tin only, with gum as the thickener; and others, a mixture of red liquor, alum, and protochloride of tin, thickened with either flour or starch.

Blue.—1. The following topical blue is sometimes grounded in by the block, for light goods, after all or most of the other colours have been applied. Being easily washed out, it is not used except with fugitive colours, and in cases where it would be inconvenient to apply the mixture for steam blue.

1 pound of yellow prussiate of potash,
1½ gills of solution of nitrate of iron of 80° Tw.,
3 gills of perchloride of tin of 100°,
1 gallon of water, and
1¼ pounds of starch.

The prussiate of potash is first dissolved in the water, and with this solution the starch is boiled briskly for a few minutes. When the mixture is cooled, the nitrate of iron and perchloride of tin are added. The blue colour is derived from Prussian blue (see page 256).

2. Indigo communicates a faster blue, so far as

the action of soap and alkalies is concerned, than Prussian blue; but the latter possesses considerably more brilliancy than the former in its ordinary state. As a topical colour, indigo is applied in the form of indigotin, or the hydruret of indigo-blue (see page 244); the deoxidizing agent employed to produce the indigotin being either metallic tin, or the red sulphuret of arsenic (red orpiment, or red arsenic). Until within a few years, almost the only solution of indigo employed as a topical colour was that known as "pencil blue;" which is prepared by mixing with water, and boiling together, about equal parts of ground indigo, orpiment, and quick-lime, and when the mixture is withdrawn from the fire and become lukewarm, adding about as much carbonate of soda as of orpiment previously introduced. The clear liquor when thickened with gum was applied to the cloth by a pencil, or by the block charged with the colour by a particular contrivance to prevent as much as possible the access of air to the sieve.

3. A much more convenient way of effecting the conversion of indigo-blue to white indigo, through the action of the same deoxidizing agent, is to mix the ground indigo with a solution (previously made) of red arsenic in perfectly caustic potash or soda, adding as much more caustic alkali as is necessary to keep the white indigo in a state of solution. In this way, the inconvenience arising from the sediment of lime and excess of orpiment is avoided.

Pencil blue contains a considerable excess of the deoxidizing agent, which is necessary on account of the rapidity with which indigo-blue is deposited from all solutions of indigotin when freely exposed to the air. With a smaller proportion, the indigo-blue might be deposited in an insoluble state on the surface of the cloth before sufficient time is allowed for the solution of indigotin to penetrate to the interior of the fibre. This inconvenience may be partly surmounted by directing a jet of coal-gas against the printing-roller, and a short length of the cloth passing from the roller.

The construction of the cylinder machine, by which pencil blue is applied, differs slightly from that represented in figure 39, page 336. The cylinder *c* is dispensed with, the engraved roller itself dipping an inch or two into the colour mixture; and the roller is cleaned from the superfluous colour by revolving in close contact with one of the sides of the colour-troughs, which thus acts as the "doctor."

4. The deoxidizing agent employed for reducing or affording hydrogen to the indigo in the preparation now commonly substituted for pencil blue, is metallic tin. One equivalent of the metal becomes oxidized, in the presence of a caustic alkali, at the expense of two equivalents of water, the hydrogen of which unites with the indigo. To prepare such a mixture fit for application by the roller, the materials may be employed in the following proportions:

4 pounds of ground indigo,
4 quarts of water,
2½ quarts of solution of caustic soda of 70° Tw.,
3 pounds of granulated tin.

The indigo is first intimately mixed with the water, the tin and alkali are afterwards added, and the mixture is heated to the boiling point, then taken off and stirred until a drop, placed on a glass plate, appears of an orange-yellow colour. To this solution is afterwards added a mixture of a solution of chloride of tin at 120° Tw. with an equal measure of muriatic acid, until the free alkali is completely neutralized, and an olive-coloured precipitate falls. The mixture is then well stirred, and added to strong gum-water to the required shade.

For some purposes, the free alkali is neutralized by tartaric acid, and from half a gill to a gill of the solution of tin is afterwards added.

It is evident that the above preparation contains white indigo in an insoluble state; in a form, therefore, unable to enter the interior of the fibres. To dissolve the white indigo and allow it to be absorbed, the printed cloth is passed through a solution of carbonate of soda of spec. grav. 8° or 10° Tw., and at the temperature 80° or 90° Fahr. On afterwards exposing the cloth to the air, the solution of white indigo, now within the fibres, absorbs oxygen and affords a precipitate of indigo-blue.

Steam colours.—Very few colours attach themselves firmly to the cloth by being merely printed on together with the mordant; but if a cloth thus printed is exposed for a short time to the action of steam, an intimate combination takes place between the tissue, colouring matter, and mordant. Before the printed cloth is exposed to steam, the colouring matter may in general be easily removed by washing with pure water; but afterwards it is attached to the tissues almost as strongly as in any other style of printing, presenting, moreover, a brilliancy and delicacy hardly attainable by any other process. Printing by steam is one of the most important of modern improvements in calico-printing; it is practised not only on goods of cotton, but also on silk, woollen cloths, and chalys.

The brilliancy and permanency of almost all steam colours are greatly increased by impregnating the cloth with a solution of tin, or, for some styles, with a solution of acetate of alumina, previous to the application of the colours. The solution of tin now commonly used for this purpose is the *stannate of potash*, which is, when properly made, a solution of peroxide of tin in caustic potash (see page 73); this preparation sometimes contains protoxide of tin, but the stannate containing the peroxide only is preferred. This alkaline solution is not nearly so injurious to the cotton fibre as the perchloride.

After having been padded in the solution of stannate of potash, the pieces of cotton are usually passed through a cistern containing a solution of muriate of ammonia, to produce a precipitate of peroxide of tin. Some printers employ very dilute sulphuric acid instead of a solution of muriate of ammonia, but the latter is decidedly preferable.

To the cloth thus prepared, or occasionally without any preparation except bleaching, the solutions of the mixed colouring materials and mordants, properly thickened, are applied either by the roller or block. Steam colours are chiefly grounded in by the block to cloths which have been already printed and finished off according to the other styles of work, particularly the madder style. The following recipes will afford examples of the principal mixtures which are applied to cotton as steam colours; some of them may also be applied to silk and woollen goods, but for this purpose the proportions of the materials generally require to be varied. The mordant most frequently used for steam colours is red liquor, mixed with oxalic or some other acid to prevent the precipitation of the compound of colouring matter and mordant.

Steam black.—The first of the mixtures following is best adapted for the roller, the other for grounding in by the block:

No. 1.

1 pint of red liquor of 18° Tw.,
2 pints of iron liquor of 24° Tw.,
1 gallon of logwood liquor of 8° Tw.,
1¾ pounds of starch,
1½ pints of pyroligneous acid of 7° Tw.

All these materials may be mixed promiscuously and then boiled for a few minutes to form a mucilage. The cotton requires to be steamed about thirty minutes.

No. 2.

3½ pints of peachwood liquor of 6° Tw.,
7 pints of logwood liquor of 6° Tw.,
12 ounces of starch,
14 ounces of British gum,
3 ounces of sulphate of copper,
1 ounce of copperas,
3 ounces of a neutral solution of pernitrate of iron, made by mixing one pound of acetate of lead with three pounds of the common acid nitrate of iron of 122° Tw.

If intended for goods of silk and wool, four ounces of extract of indigo should be added.

The logwood liquor and peachwood liquor are mixed and divided into two equal portions, one of which is boiled for a short time with the starch, and the other with the British gum. The two liquids are afterwards mixed, and the remaining ingredients are added; the nitrate of iron being introduced last, and not before the mixture is cold.

Steam red.—The best steam red for cotton is obtained by decoction of cochineal, with oxalic acid and protochloride of tin. The mixture obtained according to the following receipt may be applied either by the roller or block:

1 gallon of cochineal liquor of 6° Tw.,
1 pound of starch,
3 ounces of oxalic acid,
4 ounces of cryst. protochloride of tin.

The cochineal liquor is first boiled with the starch for a few minutes; when the mixture is half cold, the oxalic acid is added, and as soon as the acid is dissolved the salt of tin is introduced.

A cheaper but less brilliant steam red, much used by some printers, is prepared by substituting peachwood liquor for cochineal liquor in the above.

Steam purple.—To a gallon of red liquor of 18° Tw., heated to about 140° Fahr., three pounds of ground logwood are added; the mixture is well stirred for about half an hour, and then strained through a cloth filter, the residue on the filter being washed with two quarts of hot water, which are received into the first liquid. The mixture thus obtained may be diluted with water, according to the shade of colour required; for a moderate depth, one measure may be mixed with three of water, and thickened with starch, flour, or gum. This preparation may be applied either by block or roller.

Steam yellow.—Either decoction of Persian berries, decoction of quercitron, or decoction of fustic, may be used as a steam yellow, but the first is most commonly employed at present.

No. 1.

1 gallon of berry liquor of 4° Tw.,
5 ounces of alum, thickened with about
14 ounces of starch.

No. 2.

1 gallon of berry liquor of 4° Tw.,
1½ gill of red liquor of 18° Tw.,
2 ounces of crystals of protochloride of tin, and about
14 ounces of starch.

The mixture made according to the following receipt affords a darker shade than either of the preceding:

No. 3.

1 gallon of a mixture of equal measures of decoction of Persian berries at 15° Tw., and of decoction of fustic at 15° Tw.,
14 ounces of starch,
7 ounces of alum,
7 ounces of crystals of protochloride of tin.

The decoctions of the dye-stuffs are mixed with the alum and starch, and heated until properly thickened; the mixture should be soon withdrawn from the fire, and when cold mixed with the salt of tin.

The preparation made as No. 2 will probably be found superior to either of the others for cotton goods. The steaming for No. 3 must be continued only a short time, else the fibre of the cotton would be apt to become corroded by the salt of tin. This preparation is better adapted (as a steam colour) for fabrics of wool and silk than for those of cotton, but it may be advantageously applied to cotton as a spirit or wash-off colour (page 147).

The orange stripe in the specimen annexed (No.

No. 10.

10) is also produced by decoction of Persian berries, the mordant being protoxide of tin only.

A convenient mixture for producing this colour is the following:

1 gallon of berry liquor made from three pounds of berries to the gallon, and
4 ounces of cryst. protochloride of tin. Boil together for a few minutes and thicken with
3 to 4 pounds of British gum or 1 pound of starch.

The cloth may be steamed and washed in the usual manner, but this colour becomes strongly attached by merely ageing the cloth for two or three days, and then passing it through hot chalky water.

Steam blue.—A very beautiful steam blue may be communicated to cotton and woollen goods by means of a mixture of yellow or red prussiate of potash, with tartaric, oxalic, or sulphuric acid, and alum or perchloride of tin. If for applying to cotton goods, alum is used; but if for woollen fabrics, perchloride of tin is preferable. The blue in the annexed specimen (No. 11) was produced by such a process.

No. 11.

For printing on cottons by the roller, either No. 1 or No. 2 of the following mixtures may be used:

No. 1.

1 gallon of water,
$1\frac{1}{4}$ pounds of yellow prussiate of potash,
3 to 4 ounces of alum,
5 to 6 ounces of oil of vitriol,
$1\frac{1}{2}$ pounds of starch.

No. 2

1 gallon of water,
$1\frac{1}{4}$ pounds of yellow prussiate of potash,
3 to 4 ounces of alum,
10 to 12 ounces of tartaric acid,
$1\frac{1}{2}$ pounds of starch.

The starch and prussiate of potash are boiled in the water, and when the mixture is withdrawn from the fire and cooled, the sulphuric or tartaric acid and alum are introduced. The mixture made as No. 2 affords a more lively colour than that made as No. 1, but the latter is least expensive.

No. 3.

1 gallon of water,
3 to 3½ ounces of alum,
1½ to 2 ounces of oxalic acid,
3 to 4 ounces of tartaric acid,
20 ounces of gum,
12 ounces of yellow prussiate of potash.

The gum, acids, and alum may be first dissolved in the water with the assistance of heat, and when the mixture is quite cold, the prussiate of potash is added.

The time necessary for steaming cottons printed with either of these preparations is about thirty minutes. When withdrawn from the steaming cylinder or chamber, the goods present, if *yellow* prussiate of potash is used, a blueish-white colour, which changes to deep blue on exposure to the air for a couple of days. The chemical change by which the colour is produced during the exposure to air depends on the absorption of oxygen or the removal of hydrogen; as is evident from the circumstance, that if the goods are passed through a solution of bichromate of potash as soon as withdrawn from the steaming cylinder or chamber, the blueish-white changes to deep blue immediately. If the *red* prussiate of potash is employed instead of the yellow prussiate, the cloths acquire the proper blue colour during the steaming, and the depth of the colour is not sensibly increased by exposure to air or to a solution of bichromate of potash.

The blue colouring matter produced in these processes is a variety of Prussian blue, formed through the decomposition of hydroferrocyanic acid set at liberty by the action of the more powerful acids present on the prussiate of potash. When an aqueous solution of pure hydroferrocyanic acid is gently heated and exposed to the air, the acid suffers decomposition with formation of hydrocyanic or prussic acid, and Prussian blue, which precipitates. Assuming the composition of the Prussian blue thus formed to be the same as that produced by mixing a solution of yellow prussiate of potash with a solution of a salt of the peroxide of iron, (which contains cyanogen and iron in the proportion of nine equivalents of the former to seven equivalents of the latter,*) the decomposition which the hydroferrocyanic acid experiences appears to be after the following manner: seven equivalents of the acid, containing twenty-one equivalents of cyanogen, seven equivalents of iron, and fourteen equivalents of hydrogen, afford, 1°, one equivalent of Prussian blue, containing seven equivalents of iron and nine equivalents of cyanogen; 2°, twelve equivalents of hydrocyanic acid; and 3°, two equivalents of hydrogen to be removed by an oxidizing agent. This decomposition may be expressed more simply in symbols; thus,

* The prussiate of potash, which enters into the composition of this variety. Prussian blue, may be neglected in the above calculation.

7 eqs. of hydroferrocyanic acid ($H_2 + Fe\ Cy_3$) or	H_{14}	Fe_7	Cy_{21}	produce
1 eq. Prussian blue		Fe_7	Cy_9	
12 eqs. hydrocyanic acid	H_{12}		Cy_{12}	
2 eqs. hydrogen	H_2			

Such we may suppose to be the decomposition which takes place when an aqueous solution of hydroferrocyanic acid is heated with exposure to the air. That the reactions which occur in the steam blue process are somewhat different from the above, however, is pretty evident from the circumstance that the colour does not appear until the cloth is exposed to a source of oxygen, although the acid is certainly decomposed during steaming, as is manifest from the odour of hydrocyanic acid then developed. According to another, and a more consistent, view of these changes, the blueish-white compound on the steamed cloth, before being exposed to the air, is the same as the precipitate which falls on mixing a solution of yellow prussiate of potash with a solution of a salt of the protoxide of iron. This precipitate contains, besides a certain proportion of prussiate of potash, iron and cyanogen in an equal number of equivalents. When exposed to the air, it absorbs oxygen and becomes deep blue; the oxygen thus absorbed combines with a portion of the iron in the precipitate, forming peroxide of iron, which remains as an essential part of the Prussian blue.

As the blueish-white precipitate contains a compound of an equal number of equivalents of iron and cyanogen united with prussiate of potash, it may be formed from a mixture of prussiate of potash and hydroferrocyanic acid, with the separation of nothing more than hydrocyanic acid; thus,

From 9 eqs. of hydroferrocyanic acid	=	H_{18}	Fe_9	Cy_{27}
Deduct 18 eqs. of hydrocyanic acid	=	H_{18}		Cy_{18}
There remains			Fe_9	Cy_9

On exposure to the air, this compound of iron and cyanogen, the probable constitution of which is represented by the formula $Fe_6 + 3(Fe\ Cy_3)$ absorbs three equivalents of oxygen, and thereby affords a compound of peroxide of iron with the variety of Prussian blue noticed in the preceding page. The formula for this compound is $Fe_2\ O_3 + (Fe_4 + 3(Fe\ Cy_3))$.

The reactions which occur when the red prussiate of potash is employed are different, the acid liberated from that salt by the action of the stronger acids not having the same composition as hydroferrocyanic acid. The composition of hydroferridcyanic acid (the acid liberated from the red prussiate) is such as to allow of the decomposition of the acid into Prussian blue, hydrocyanic acid, and cyanogen, without the interference of atmospheric air or any other source of free oxygen.

In its present form, this beautiful colour has not been long in general use for application to calicos. The colour obtained by the mixture formerly employed, consisting of prussiate of potash with tartaric or sulphuric acid, without any addition of perchloride of tin or alum, is always lighter in shade and less vivid than that obtained with such an addition, however concentrated the solution of prussiate of potash. The acids in the mixture, including the sulphuric acid of the alum in combination with alumina (namely three equivalents for one equivalent of alum), should be in sufficient quanity to neutralize one equivalent of alkali for every two-thirds of an equivalent of prussiate of potash; or to saturate 5·9 ounces of anhydrous potash for 18 ounces of the prussiate.

Steam green.—A very good steam green may be communicated to cotton goods by combining the materials for producing a yellow, with the preceding mixture for steam blue; thus,

1 gallon of berry liquor made from a pound and a half of Persian berries (or of 4° Tw.),
12 ounces of yellow prussiate of potash,
3 to 4 ounces of crystals of protochloride of tin,
5 to 6 ounces of alum,
3 to 4 ounces of oxalic acid.
Thicken with gum.

The oxalic acid, the muriatic acid derived from the salt of tin, and the sulphuric acid united with alumina in the alum, should form, together, one equivalent, or a quantity sufficient for the saturation of one equivalent of a protoxide for every two-thirds of an equivalent of the prussiate. The time required for steaming this colour is about thirty minutes.

After the colour mixtures are printed on, the calico is dried in a warm atmosphere for two days or thereabouts before being exposed to the action of the steam. Different methods of applying the steam are practised in different print-works. In some the goods are introduced into a large stout deal box, the lid of which is made very nearly steam-tight by edges of felt. The steam is admitted near the bottom by a thickly perforated pipe which traverses the box. For the deal box is sometimes substituted a small chamber built of masonry, about four or five feet in length, by three feet in width, and three feet in height. The cloth is suspended free from folds, on strings across the chamber.

The most common method of applying the steam is the following. Three or four pieces of the printed and dried calico are stitched together at the ends and coiled round a hollow cylinder of copper, about three feet in length and four inches in diameter, and perforated with holes about one-twelfth of an inch in diameter and half an inch distant from each other. One of the ends of the cylinder is open, to admit the steam; the other is closed. The calico is prevented from coming immediately into contact with the cylinder by a roll of blanket stuff, and is covered with a piece of white calico tightly tied around the roll. During the lapping and unlapping of the calico the column is placed horizontally in a frame, in which it is made to revolve; but during the steaming it is fixed upright, and supplied with steam through its bottom from the main steam boiler of the works, the quantity admitted being regulated by a stopcock. During the whole process the temperature of the steam should be as near 211° or 212°, as possible: the condensation which takes place below that degree is apt to cause the colours to run; but a higher temperature is also injurious, as a slight condensation, sufficient to keep the goods always moist, is essential to the success of the process. The steaming is continued for from twenty minutes to three quarters of an hour, according to the nature of the stuff and the colouring mixture. The usual time with cottons is twenty-five minutes, and with de laines about thirty or thirty-five minutes. The time required for steaming cotton goods by the chamber is longer than what is required by the column, being generally about an hour. When the steam is cut off, the cloths should be immediately unrolled to prevent any condensation: they are then soft and flaccid, the material used as a thickener for the colours being in a semi-fluid state; but on exposure to the air for a few seconds only, the thickener solidifies, and the goods become perfectly dry and stiff. After the pieces have been aged for a day or two, the thickener is separated by a gentle wash in cold water.

To produce with steam colours only such a pattern as the annexed (No. 12), containing a design in lilac, pink, red, yellow, black, and dark orange red, the cloth may be printed by the five-colour machine in the following manner:

No. 12.

By the first roller, with a mixture of logwood liquor, starch, and solution of tin for producing the lilac;

By the second and third rollers, with the mixtures for the pink and red (see page 155), one containing weaker cochineal or peachwood liquor than the other;

By the fourth roller, with the mixture for the yellow (see page 156);

By the fifth roller, with the mixture for steam black (see page 154).

The dark orange red results from the mixture of the red with the yellow. After being steamed, the cloth is aged in a warm room for two days and two nights, and then washed at the rinsing machine.

The style following, for producing a design in black, red, brown, green, and yellow on a white ground, is a combination of the madder style with a topical brown and steam colours, which is susceptible of a great variety of interesting modifications.

1. The cloth is printed by the three-colour machine in the following manner: with iron liquor, for black, by the first roller; with red liquor by the second roller, and with catechu brown (page 145) by the third roller.

2. After being printed, the cloth is aged for two days, dunged, dyed in the madder-beck, and cleared.

3. The cloth is lastly printed by the block with the mixtures for steam green (page 163), and steam yellow (page 156), then steamed, aged, and washed.

By a similar series of operations, a design may be imparted in black brown, lilac, pink, green, blue, orange, and yellow, on a white ground. The cloth is first printed by the four-colour machine with iron liquor of two strengths, one for the black, the other for the lilac; with red liquor for the pink, and with the mixture for catechu brown (page 145). After being aged, dunged, dyed with madder, and cleared as usual, the cloth is printed by the block with the mixtures for steam blue (page 158), and steam yellow (page 156), and then steamed in the ordinary manner. To produce the orange, the steam yellow is printed on a part of the pink, and the green results from the mixture of some of the yellow with the blue.

The specimen No. 10, page 157, is an example of the combination of madder colours with steam colours; for the red and chocolate stripes, the cloth was printed with red liquor and the mixture of red liquor with iron liquor, and after dunging, dyeing, and clearing in the usual manner, the mixture for steam orange was applied by the block.

3. MINERAL COLOURING MATTERS.

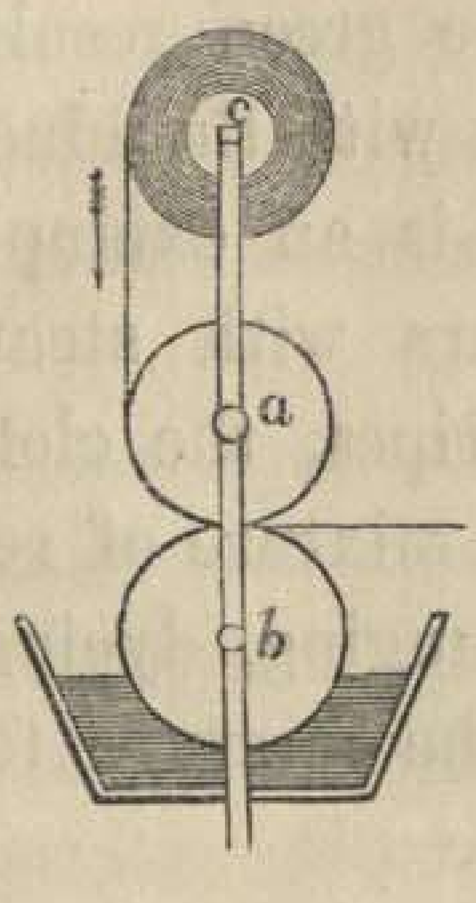
Mineral colouring matters are adapted, not only to the production of designs on a white or coloured ground, but also to form a ground for the reception of a design in other colours. To impart the colour to the entire surface of the cloth, the latter may be impregnated successively, by the padding machine, with the two solutions necessary to produce the colour, or else the cloth may be padded in one of the solutions and be afterwards winced in the other.

To produce a design in a mineral colouring matter on a white or coloured ground, the cloth is usually first printed with one of the solutions, and then either padded or winced in the other.

The common "padding machine," by which a cloth is uniformly imbued with a liquid, is much the same as the starching machine (fig. 37, page 108), the thickened liquid being contained in the trough *a*.

A simpler padding machine is employed in some print-works, of which fig. 41 is a representation: *a* and *b* are two cylinders revolving in close contact; *b* is covered with blanket stuff, and dips partly into a trough which contains the liquid slightly thickend. The calico is first rolled around the cylinder *c*, and then passed in the direction of the arrow between the cylinders *a* and *b*. As soon as the calico is padded, it is dried hard, by exposure to a temperature, of 212° or thereabouts, either by being drawn over a series of sheet-iron boxes heated by steam, or through the steam drying machine described at page 325, or through the hot-flue. If the colour is to be applied to the face of the cloth only, and not to both face and back, the common printing machine with a roughened roller is substituted for the padding machine.

Fig 41.



Prussian blue.—More than one method of applying this colouring material to cloth has already been noticed; another is by the consecutive application of either yellow prussiate of potash and a salt of the peroxide or protoxide of iron, or red prussiate of potash and a salt of the protoxide of iron. The latter method is very rarely practised. To impregnate the entire surface of a piece of cloth with Prussian blue, it may be treated in the following manner :

1° Pad in a solution of acetate and sulphate of iron made by adding three pounds of acetate of lead to a solution of four pounds of copperas in a gallon of water, decanted from the precipitated sulphate of lead and diluted to the density 2° or 3° Tw.

2° Dry the cloth, and then wince it in warm chalky water.

3° Wince it in a solution of a pound of yellow prussiate of potash in forty gallons of warm water, to which are added four ounces of oil of vitriol.

To produce a design in Prussian blue by this style of work, the cloth may be printed with the mixed solution of acetate and sulphate of iron, made as above, of spec. grav. 4° or 5° Tw., thickened with gum and "sightened" by the addition of a little prussiate of potash. After being aged, the cloth is winced in chalky water, cleaned, and winced until it acquires the desired shade in a solution containing three or four ounces of prussiate of potash, and one fluid ounce of muriatic acid per piece.

Chrome-yellow.—The yellow and orange in the specimen annexed (No. 13) are produced by the two chromates of lead, chrome-yellow and chrome-orange.

To impart a ground of chrome-yellow to a piece of calico, the cloth should be padded with a solution of two pounds of acetate of lead in a gallon of water

No. 13.

containing a little size, then dried, passed first through a weak solution of carbonate of soda, and afterwards through a solution of bichromate of potash. Rinse and dry.

To apply chrome-yellow topically, the cloth may be printed with a solution containing both acetate and nitrate of lead (from seven to ten ounces of each to the gallon) thickened with starch. After being printed and dried, the cloth is winced first in a weak solution of carbonate of soda, and afterwards in a solution of bichromate of potash containing about two ounces per piece. To clear the whites, the cloth may be winced in water slightly acidulated with muriatic acid.

Chrome-orange.—A ground of chrome-orange may be communicated to a piece of cotton by first applying chrome-yellow in the ordinary manner, and then exposing the cloth to boiling lime-water, which withdraws a portion of the chromic acid from the chrome-yellow and leaves chrome-orange: thus,

1. Pad the cloth twice in a saturated solution in water of acetate and nitrate of lead, in the proportion of a pound of the nitrate to a pound and a quarter of the acetate.* Dry in the hot-flue.

2. Wince in weak milk of lime for a few minutes.

3. Wince in a warm solution of bichromate of potash containing five or six ounces per piece; and lastly,

4. Wince in boiling milk of lime. Rinse and dry.

To produce a design in chrome-orange on a white ground, the cloth may be printed with a saturated solution of acetate and nitrate of lead (as above) thickened with British gum; after being dried, it is passed through a solution of sulphate of soda to fix the oxide of lead in an insoluble state, then well washed in water, and winced in a warm solution of bichromate of potash. It is afterwards rinsed, and passed through boiling milk of lime to convert the chrome-yellow into chrome-orange.

A design in chrome-yellow on a chrome-orange ground may be obtained by printing an acid on the orange ground, so as to withdraw the excess of oxide of lead from the subchromate (orange), and thus form the neutral chromate (yellow). The specimen No. 13 was produced in this way; the blue and black are merely spirit colours.

Different shades of green are given to cotton goods by a mixture of chrome-yellow with Prussian blue. The colouring materials may be applied consecutively or at once from mixed solutions; the cloth being

* Water is capable of dissolving nearly twice as much of a mixture of acetate and nitrate of lead, in the proportion of single equivalents, as of either of the salts separately.

first padded, in the latter case, with a mixture of acetate of iron and nitrate of lead, and afterwards winced in a solution of prussiate of potash and bichromate of potash with a small quantity of muriatic acid.

To obtain a design of a green colour by conjoining chrome-yellow with indigo-blue, the cloth may be printed with a solution of from two pounds to two pounds and a half of nitrate of lead in a gallon of the neutralized mixture of white indigo with solution of tin prepared as described at pages 151, 152. After being printed, the cloth is passed, first, through a warm solution of carbonate of soda to fix the blue and oxide of lead, and afterwards through a solution of bichromate of potash to raise the yellow.

Iron buff.—The solutions of iron in common use for iron buff are the pernitrate and a mixture of the acetate with the protosulphate, obtained by adding from one part to three parts of acetate of lead (pyrolignite) to three parts of copperas. Double decomposition takes place between the acetate of lead and a portion of the copperas with formation of acetate of iron and sulphate of lead. For producing light shades, alum is sometimes added, together with a little carbonate of soda to take up a portion of the acid of the alum. Acetate of lime is frequently substituted for acetate of lead, in the preparation of "buff-liquor."

The buff colour in the specimen following (No. 14) is produced by iron buff.

To impart a buff ground, the pieces are padded in

No. 14.

buff-liquor of any strength between 2° and 10° Tw., according to the shade of colour desired, then dried by being drawn either through the hot-flue or over iron boxes filled with steam, and aged for one or two days. Some printers then wince the pieces in water containing some chalk, and afterwards pass them through a solution of carbonate of soda; but it is much better to pass them at once through a solution of caustic soda, or through milk of lime.

During the ageing of the padded goods the salts of the protoxide of iron became subsalts of the peroxide, which are decomposed in the alkaline or calcareous solution, the acids being withdrawn by the alkali while the peroxide of iron becomes fixed on the cloth.

To obtain an iron buff figure, the pieces may be printed with a buff-liquor of any strength between 10° and 30° Tw. thickened with either gum, calcined farina, salep, or British gum. After being dried and aged, the pieces are passed directly through a solution of caustic soda, or else through milk of lime.

Manganese bronze.—The brown ground of the specimen annexed (No. 15) is produced by manganese bronze or peroxide of manganese.

No. 15.

A solution of manganese sufficiently pure for producing the bronze, may be obtained from the residue of the process for chlorine, by saturating the remaining free sulphuric or muriatic acid with chalk, allowing the precipitate to settle, and decanting and concentrating the clear supernatant liquid. The chalk serves not only to saturate the free acid, but to precipitate peroxide of iron from the soluble salts of that oxide which this bye-product always contains. Lime has been recommended for this purpose instead of chalk, but it is never employed on the large scale, as an excess would decompose the salts of manganese as well as those of iron; an excess of chalk however, is without action on the manganese salt.

A purer solution of manganese is prepared by heating the residue of the chlorine process with more black oxide of manganese until the evolution of chlorine almost ceases, and then adding, either chalk, or freshly precipitated carbonate of manganese, until the liquid becomes colourless. Having been allowed to settle, the solution is decanted and concentrated by evaporation.

To impart a dark bronze ground such as that in the above specimen, the strength of the solution of chloride of manganese may be about 26° Twad. For lighter shades, the solution may be made as weak as 4° Twad.

After having been padded and dried, the goods are passed through a cold caustic ley, whereby protoxide of manganese becomes precipitated on the cloth. On exposure to the air, the protoxide soon absorbs oxygen, passing into the state of the brown peroxide; but the peroxide may be produced immediately by wincing the goods in a solution of chloride of lime or chloride of soda as soon as they are taken out of the caustic ley. The common practice is to expose the pieces to the air until they acquire a good full colour, and then to complete the peroxidation of the manganese by a dilute solution of chloride of lime.

Peroxide of manganese is very seldom applied as a figure on a white ground. The solution of the chloride used for this purpose may have a density about 16° Tw. and be thickened with from two pounds to two pounds and a half of gum to the gallon. A small quantity of tartaric acid is a useful addition to such a solution. The printed and dried cloth is drawn through a caustic ley, exposed to the air, and winced in a solution of chloride of lime as above.

Scheele's green—To obtain a ground of Scheele's green (arsenite of copper), the cloth is padded two or three times with a solution of nitrate of copper, or else with a mixture of the sulphate and acetate containing a little size, and after being dried, is winced in a dilute solution of a caustic alkali, to fix the oxide of copper. The cloth is then rinsed in water and winced in a dilute solution of arsenious acid, or else in a solution of arsenite of soda.

For the manner of applying a few other mineral colours, namely, antimony orange, arseniate of chromium, orpiment, and prussiate of copper, see page 38, *et seq.*

Mineral colours are frequently combined with steam and madder colours in the same design. When this is the case, the madder colours are always applied first, the mineral colours next, and the steam colours last.

The following method of procuring a design in black, purple, two shades of red, two shades of buff, green and yellow, on a white ground, is an example of the combinations of mineral colours with madder and steam colours:

1. Print the cloth by the four-colour machine with the mordants for black, purple, and two reds (see pages 137 and 138);

2. Age, dung, dye in the madder-beck, clear and dry;

3. Print by the two-colour machine (or else by

blocks, according to the design) with buff-liquor of two strengths, thickened with starch or British gum;

4. Wince the cloth, after being aged, in milk of lime, to raise the buff, and rince the water;

5. Dry and print by blocks with the mixtures for steam blue (page 158), and steam yellow (page 156);

6. Age, steam, and rinse.

A pleasing pattern may be obtained by combining in one design, on a white ground, figures or bars in different shades of iron buff, with a figure or stripe in steam blue. The buffs are first applied in the usual manner.

4. RESIST STYLE.

The object of the resist style of work is to produce a white or coloured design on a coloured ground by the topical application, in the first place, of a substance called the *resist*, *reserve*, or *resist paste*, which has the property of preventing the attachment or developement of colour, when the whole surface of the cloth is afterwards impregnated with a dyeing material. One class of resists, consisting of substances of an unctuous nature, acts merely mechanically; another class acts both mechanically and chemically. The latter kind are divisible into two subdivisions, according as their influence is exerted merely on the mordant or on the colouring matter itself.

1. *Fat resists.*—Resists of an unctuous nature are chiefly used for applying to goods of silk and wool,

but they may be also advantageously applied, in particular circumstances, to goods of cotton. The annexed specimen (No. 16) is an example of the

No. 16.

combination of such a style of work with madder colours and steam colours. The specimen No. 7, page 139, shews the appearance of the above in an early stage of the process. After having been printed, dyed, and cleared as already described, the red and lilac figures are covered (or overlaid) with a resist consisting, usually, of an intimate mixture of suet and gum-water.* The whole is then run over by the roller with weak iron liquor for the lilac ground, and the cloth is aged, dunged, dyed, and cleared. The mixtures for steam green and steam yellow are afterwards pegged in by blocks, and the steaming is performed in the usual manner. The mixture for the green in the above specimen is quite

* A solution of citrate of soda (obtained by neutralizing lime-juice with soda), thickened with pipe-clay and gum, might be used instead of the mixture mentioned in the text.

similar to that described at page 163; that for the yellow was made by mixing a quart of red liquor of spec. grav. $8\frac{1}{2}°$ Tw. with a gallon of berry liquor of 2° Tw.

In this style of work, however, the dyeing with madder might as well be performed at one operation, as the red and lilac mordants for the figures are not at all injured by the fat resist with which they are covered.

2. *Resists for mordants.*—The material generally used for preventing the deposition of a mordant on particular parts of the cloth is an acid or acidulous salt capable of uniting with the base of the mordant, to form a compound soluble in water and not decomposable into an insoluble subsalt during the hanging of the mordanted goods, previous to dunging and dyeing. The resist commonly employed for the iron and aluminous mordants is lemon-juice or lime-juice, or a mixture of one of these with tartaric and oxalic acids and bisulphate of potash. The thickening material is either a mixture of pipe-clay or china-clay with common gum, a mixture of British gum with gum senegal, or British gum alone. Lemon-juice or lime-juice is decidedly preferred to pure citric acid (which is the acid principle of these juices), as the mucilaginous matters in the former impede the crystallization of the acid within the pores of the cloth, and thus render it better adapted to prevent the attachment of the mordant in an insoluble form. The strength of the resist is regulated by the strength of the mordant afterwards applied; it is seldom used of a higher density than 2° Twad.

The specimen (No. 17), exhibiting a design in black, lilac and white on a lilac ground, was produced

No. 17.

by adapting the resist style of work to madder colours. The printing for such a pattern may be performed by the three-coloured machine in the following order:

By the first roller; the resist, which may be either lemon-juice or spec. grav. 2° or 3° Twad., thickened with four pounds of British gum to the gallon, or else a solution of about the same density, of tartaric and oxalic acids in weaker lemon-juice, also thickened with British gum:

By the second roller; the mordant for the black, which is iron liquor of spec. grav. 8° Twad., thickened with a pound and a half of flour to the gallon:

By the third roller; the mordant for the ground of lilac, which is iron liquor of spec. grav. 1½° Twad., thickened with four pounds of British gum to the gallon.

The application of the mordant of the ground may be made by the padding machine (fig. 41, page

168), but it is commonly done by the cylinder machine, the entire surface of the copper roller being slightly roughened or engraved in close diagonal lines, so as to enable it to afford an uniform deposit on the cloth.

The operations of ageing, dunging, dyeing, and clearing are conducted in much the same manner as if the acid resist had not been applied. It is usual, in this style of work, to add a small quantity of chalk to the dung-beck, in order to counteract the effects of the free acid in the resist.

Iron liquor may be resisted or prevented from affording a deposit of insoluble subsulphate during the ageing, by a process somewhat different from the above, the resisting agent being protochloride of tin (commonly called salts of tin), instead of a free acid or an acidulous salt. A mixture of protochloride of tin and iron liquor does not afford a deposit of a subsalt of iron during the ageing of cottons printed with the mixture, probably through the occurrence of a double decomposition with formation of acetate of tin and chloride of iron. The latter compound does not afford an insoluble precipitate during the ageing, and may be entirely removed from the cloth by washing.

When a piece of cotton cloth is printed with a solution of salts of tin by the first roller of a two-colour machine, and with iron liquor by the second roller, over the parts printed by the first roller, such a mixture as the above is of course formed wherever the salt of tin had been applied, and no subacetate of iron is deposited there during the ageing.

The protochloride of tin, however, is never applied in this way with a view of producing a white figure on a coloured ground; it is commonly mixed with red liquor, as the deposition of the insoluble sub-sulphate of alumina from that preparation is not interfered with by the protochloride. After a piece of cloth thus printed has been aged, dunged, dyed in the madder-beck, and cleared, it therefore presents a red figure surrounded by purple or lilac. It is to be observed that this method of procedure is only followed when a better definition of the red design is required than could be attained by leaving a blank figure in the roller for the iron liquor, and afterwards printing the red liquor on the white parts either by a second roller or by the block. To resist weak iron liquor and impart the mordant for a full red with madder, the mixture may have the following composition:

1 gallon of red liquor of 18° Twad.,
4 oz. crystals of protochloride of tin; with a sufficient quantity of British gum or a mixture of British gum and starch as the thickener.

To obtain a design in full red and black on such a lilac ground as the specimen No. 16, page 178, contains, the cloth is printed with strong iron liquor for the black, with the above mixture for the red, and with iron liquor of 1° Twad. for the lilac; after which it is aged, dunged, dyed, &c. in the usual manner. A great variety of pleasing effects may be produced by combining this kind of work with steam or topical colours, the iron liquor not being applied as a ground, but as a design extending on each side of the red figure, and on the parts left white the steam colours are applied, after dyeing with madder and clearing.

Another material, much used as a resist for red liquor and iron liquor, is a solution of citrate of soda, prepared by neutralizing lime-juice of about 4° Twad. with soda, thickened with a mixture of gum and pipe-clay. The action of this resist may probably be referred to the tendency of citric acid, like oxalic acid and a few others, to form a double salt with peroxide of iron or alumina and an alkali, which affords no precipitate of alumina or oxide of iron during the ageing. In this case a portion of the alkali in the neutral citrate is withdrawn by the acetic acid in the mordant, an acid citrate of soda being thus formed. Neutralized lime-juice of 4° Tw. has about the same resisting power as the unneutralized juice of 2° Tw.

The principal use of neutralized lime-juice as a resist for iron liquor is to protect figures previously applied in madder-colours; for which purpose the free acid is quite inapplicable, as it would dissolve the mordant on the cloth in combination with the colouring matter. If the dyeing of the cloth with madder for such a pattern as that of the specimen No. 16, page 178, is performed at two operations, neutralized lime-juice is generally preferred to the fat resist for protecting the red, lilac and white figures of the specimen No. 7, page 139; but if the maddering is to be completed at one operation, the fat resist must be used.

3. *Resists for the colouring matter.*—The production of a white or coloured pattern on a coloured

ground by the direct actiou of a resist on a colouring matter, is chiefly practised with indigo, at least in the printing of calicos. The substances most commonly employed for this purpose are salts of the black oxide of copper, particularly the sulphate and the acetate. The other substances employed as resists for indigo are sulphate of zinc, chloride of zinc, chloride of mercury (corrosive sublimate), and a mixture of corrosive sublimate and binarseniate of potash. None of these are in common use except sulphate of copper, acetate of copper, and sulphate of zinc.

The ordinary course of operations practised in this style of work, with the view of producing merely a white pattern, are the following:

The resist, mixed with unctuous matters and properly thickened, is first printed on such parts of the cloth as are not to absorb the indigo, and the goods are suspended for one or two days (according to the composition of the resist) in a chamber at common temperatures, and not very dry. The pieces are then fixed on a frame and dipped into the indigo vat, which contains, in solution, the colourless hydruret of indigo, or indigotin (see page 28). The solution of indigotin is immediately absorbed by the cloth on all parts where the resist had not been printed, which parts become deep blue when the cloth is afterwards exposed to the air, the soluble indigotin passing into the state of insoluble indigo-blue through the absorption of oxygen. But wherever the resist had been applied, the solution of indigotin is not absorbed by the cloth, partly on account of the unctuous matters contained in the resist, but chiefly from the action of the metallic salt on the indigotin in solution, by which either indigotin or else indigo-blue becomes precipitated before the solution reaches the interior of the fibre, and being precipitated, the indigo is rendered incapable of being absorbed by the pores of the cloth. The indigo-blue which is formed by the resist is merely attached to the surface of the cloth, and is easily removed by washing.

The first chemical change which occurs when the cloth printed with a resist containing sulphate or acetate of copper or corrosive sublimate is dipped into the indigo-vat, is, the decomposition of the metallic salt in the resist by the alkali or lime in the vat, whereby the cupreous salts afford a precipitate of hydrated protoxide of copper (black oxide) and corrosive sublimate, a precipitate of protoxide of mercury (red oxide).* These oxides are no sooner produced than they exert an oxidizing action on the indigotin in solution, and become reduced to the state of inferior oxides. The protoxide of copper becomes the red or suboxide (which generally requires to be cleared away at the end of the process by wincing the goods in dilute sulphuric acid), and the protoxide of mercury becomes the black oxide or suboxide.

The mode of action of sulphate of zinc is somewhat different. This salt exerts no oxidizing action on the indigotin, but causes the precipitation of that substance in an insoluble state by withdrawing the lime which holds it in solution. By the reaction of the lime in the solution on the sulphate of zinc, there are also precipitated sulphate of lime and oxide of

* Commonly called the peroxide.

zinc, both of which offer a mechanical impediment to the access of the liquid to the cloth.

The sulphate of zinc resist should be used only in cases where it would not be allowable to expose the goods to dilute sulphuric acid, after having been dipped into the blue-vat, as if, for instance, a design had been previously applied in madder colours, this operation being unnecessary with the zinc salt. Corrosive sublimate is far too expensive, and also too weak, to be commonly employed as a resist for indigo, except where a very delicate figure in madder colours has to be protected.

The white pattern in the annexed specimen (No. 18) was produced by such a process as that just

No. 18.

described. For this style of work, the blue-vat or solution of indigotin may be made by mixing one hundred pounds of ground indigo, one hundred and thirty-five pounds of copperas, one hundred and seventy-five pounds of lime, and from sixteen hundred to two thousand gallons of water. The vat is fit for use two days after the materials are mixed.

For a deep blue, the cloth is dipped into the vat for ten minutes and then exposed to the air for the same length of time, and the dipping and exposure to the air are repeated until the required depth of colour is obtained.

The composition of the resist paste is varied according to the depth of colour in the blue ground. The following mixture is well adapted for dark blue:

No. 1.

3 to 4 pounds of sulphate of copper,
7 pints of water,
5 pounds of pipe-clay, china-clay, or sulphate of lead,
4 ounces of soft soap,
3 pounds of gum.

For a resist paste for light blue, the proportion of sulphate of copper may be reduced to eight ounces in a gallon of the paste. This resist we may call No. 2.

The sulphate of zinc resist, for protecting a design in madder colours as well as for preserving some white, may have the following composition:

No. 3.

4 to 5 pounds of sulphate of zinc,
2 quarts of boiling water,
5½ pounds of pipe-clay,
4 ounces of soft soap,
2 ounces of hog's lard,
2 quarts of gum senegal water, containing six pounds of gum to a gallon of water.

The sulphate of zinc is first dissolved in the hot water, and with this solution, while warm, the pipe-clay, soap, and lard are thoroughly incorporated. When the mixture is cold the gum-water is added.

Such are the methods of obtaining a white figure on a blue ground by the resist style. To procure a design in white and light blue on a dark blue ground, the cloth is first printed with the strong cupreous resist (No. 1), dipped in the blue-vat and cleaned, as if a white design only is required. After being dried, it is printed with the weaker resist containing sulphate of copper (No. 2), again dipped in the blue-vat to a lighter shade, cleared in dilute sulphuric acid, and dried.

A great variety of coloured designs on the same ground may also be obtained by combining with the resist, either one of the saline solutions capable of imparting a mineral colour, or else the mordant for a colouring matter to be applied by the madder style.

A design composed of yellow figures on an indigo ground, is very commonly and easily obtained by combining the resist with a salt of lead, and padding or wincing the cloth in a solution of bichromate of potash after being dipped into the indigo-vat and cleared. The successive operations to which a piece of calico is subjected in this kind of work are the following:

1. Printing with the mixture of resist and salt of lead, which may have the following composition:

> 1 gallon of water,
> 3 to 4 pounds of sulphate of copper,
> 1 pound of nitrate of lead,
> 1 pound of acetate of lead,
> 3 pints of a paste of precipitated sulphate of lead,
> 5 or 6 pounds of pipe-clay,
> 2 to 3 pounds of gum.

2. Hanging for one or two days in a room having a rather humid atmosphere;

3. Dipping into the indigo-vat;

4. Passing through dilute sulphuric acid;

5. Steeping in water for half an hour, and washing;

6. Wincing in a dilute solution of carbonate of soda;

7. Wincing in a solution of bichromate of potash, containing five ounces of the bichromate per piece of calico;

8. Wincing in dilute muriatic acid;

9. Washing in water.

To obtain a figure of chrome-orange instead of chrome-yellow, the calico may be first treated as above, and afterwards winced in hot milk of lime to convert the chrome-yellow into chrome-orange.

To procure a design in yellow and light blue on a dark blue ground, the cloth is submitted to the following operations:

1. It is first printed with the mixture of sulphate of copper and salts of lead for chrome-yellow, and on the parts to be light blue with a mixture of sulphate of copper and acetate of copper, formed by mixing solutions of acetate of lead and sulphate of copper, allowing the mixture to settle and decanting the supernatant liquid;

2. After being dried, the cloth is dipped into the blue-vat for the dark ground;

3. It is next passed through dilute sulphuric acid, to clear the whites of the suboxide of copper, and washed in water;

4. After being winced in a mixed solution of carbonate of soda and carbodate of ammonia, it is dipped a second time into the blue-vat for the light blue of the figure, and then washed in water;

5. It is afterwards winced in a solution of bichromate of potash, and then drawn through a cistern containing a solution of one ounce of oxalic acid and one ounce of sulphuric acid to the gallon of water.

A pattern comprising a figure of iron buff on a ground of indigo may be applied to cloth by a similar combination of the padding and resist styles, the cupreous resist being mixed with a salt of the peroxide of iron. After the ground of indigo is applied, the cloth is slightly washed, and then winced in a warm dilute solution of carbonate of soda to precipitate hydrated oxide of iron. A buff figure on a dark green ground is sometimes produced by first printing the cloth with the white resist No. 1 (page 187), then dipping into the blue-vat, and after the cloth is cleared and dried, padding it with buff-liquor, and raising the buff by carbonate of soda.

Another method of producing a coloured figure on the indigo ground is by combining with the resist paste a mordant for a vegetable colouring matter, to be applied by the madder style, after the cloth has been dipped into the indigo-vat. This kind of work, which is susceptible of a great variety of modifications, is distinguished as the *lapis* or *lazulite style*, from the resemblance of the calico thus printed and dyed to the mineral lapis lazuli. It is also known as the *neutral style*.

To obtain a red figure on the indigo ground, the cloth is printed with a resist paste composed, essentially, of red liquor, sulphate of zinc, and acetate of copper.

This resist may be made of the following materials, mixed in the order in which they are placed:

No. 1.

2 gallons of boiling water,
6 pounds of alum,
4 pounds of crude acetate of lead,
4 ounces of chalk, added in small quantities at a time, and
6 ounces of sulphate of zinc.

These materials having been thoroughly incorporated, the mixture is allowed to settle, and the clear supernatant liquid is decanted and mixed with acetate of copper and gum senegal, thus:

No. 2.

1 gallon of the above clear liquid,
3 ounces of acetate of copper,
18 ounces of gum senegal,
5 pounds of pipe-clay,
4 ounces of soft soap, and a little ground indigo for "sightening."

One half of the liquid is well mixed with the acetate of copper, pipe-clay, and soap, and the gum senegal is afterwards added, dissolved in the other half of the liquid.

After being printed with this resist, the cloth is aged for two or three days, and then subjected to the following operations:

1. Drawing by rollers once* through the blue-vat at 70° Fahr., made from the proportions of lime, copperas, and indigo mentioned at page 186, but with only eight hundred gallons of water;
2. Rinsing in water;
3. Dunging or branning;
4. Washing at the dash-wheel;

* If the cloth is exposed to the blue-vat for some length of time, the aluminous mordant is separated from the cloth by the lime in the vat.

5. Dyeing in the madder-beck, with from two to five pounds of madder per piece;

6. Clearing by boiling first in bran-water and afterwards in soap-water.

To produce a light red figure with madder, the resist may have the following composition:

4 measures of the sulphate of zinc resist paste No. 3, page 187,
1 measure of the mixture of red liquor and sulphate of zinc made as above,
1 measure of weak peachwood liquor,
1 measure of water.

For two reds the cloth may be printed with the preceding mixtures at the same time by the two-colour machine, and be treated afterwards in the manner just described.

To obtain merely a small black figure on the indigo ground the cloth may be dipped in the blue-vat to the required shade, and then be printed with the mixture for producing a topical black dye, such as pernitrate of iron, copperas, and extract of logwood (see page 144). But if the design includes figures in red and white, the black forming a more considerable portion of the figure than a mere outline, it is better to mix iron liquor of 8° or 10° Twad. with the cupreous resist, and to dye the cloth in the madder-beck after having dipped it into the blue-vat to the proper shade. A great variety of purple, lilac, and chocolate tints may also be obtained on the same ground, by combining with the cupreous resist either weak iron liquor or else mixtures in various proportions of iron liquor with red liquor, and dyeing in madder after the dipping in the blue-vat.

To impart to the blue ground a design in light blue, together with a colour capable of being applied by the madder style, the cloth may be treated as follows:

1. Print with the white resist No. 1 (page 187);

2. Dip into the blue-vat, wash, wince in dilute sulphuric acid, rinse in water, and dry;

3. Print the mixture of the mordant with the cupreous resist on a part of the white figure produced by the first resist;

4. Dip a second time into the blue-vat, to obtain a light blue on the parts not protected by the second resist, rinse in water;

5. Dung, wash, and dye in the decoction of the dye-stuff, and afterwards clear by branning.

If a white figure is required in addition to the above, the cloth is first printed with the strong white resist and dipped into the blue-vat as already described, and is afterwards printed on the protected parts, by the two-colour machine, if the design admits, with the mixture of mordant and salt of copper, and also with a mild resist such as No. 2, page 187. It is then dipped into the blue-vat and dyed in the usual manner.

To procure such a pattern as the annexed (No. 19), containing a design in orange, crimson, and white on a blue ground, the cloth is printed by the two-colour machine with the mixture of salts of copper and salts of lead (page 188) on the parts to be orange, and with a white resist on the parts to be crimson and white. After being dipped into the blue-vat and cleared in dilute sulphuric acid, it is winced in the following liquids: 1°, solution of car-

No. 19.

bonate of soda; 2°, solution of bichromate of potash; and 3°, dilute muriatic acid. It is next passed through hot milk of lime to convert the chrome-yellow into chrome-orange, rinsed, and dried, and is afterwards printed by block on parts of the white with the mixture for a topical or steam red or crimson.

The following specimen (No. 20), exhibiting a design in blue, yellow, green, red, and white on a dark chocolate ground, was produced by combining the lazulite style with a topical colour. This kind of work is distinguished as the "chocolate ground neutral style." For such a pattern the cloth is first printed (either by machine or block) with the white resist,* No. 1, page 187, on all the parts required to be yellow and white; with the mixture of red liquor,

* If a very small or well-defined white figure is required, the cupreous resist should be mixed with lime-juice and sulphuric acid or bisulphate of potash, to resist the mordant in the chocolate resist, afterwards applied as a blotch. Such a mixture is designated (not very appropriately) *neutral paste*.

No. 20.

sulphate of zinc, and acetate of copper, made as described at page 191, on the parts required to be red; and with a mixture of iron liquor, red liquor, sulphate of copper, and soft soap thickened with pipe-clay and gum, for the chocolate ground or "blotch." After having been aged for a day or two the cloth is drawn once through the indigo-vat, then washed, dunged, dyed in the madder-beck, and cleared by branning. Lastly, the mixture for a topical or steam yellow is applied by the block.

A process referable to the resist style is that by which a white figure is obtained on a ground of catechu brown. On the parts to be preserved white, the cloth is printed with a solution of citrate of soda (such as that obtained by exactly neutralizing lime-juice with caustic soda) thickened with a mixture of pipe-clay and gum; or else, what is preferred, a mixture of sulphate of zinc, pipe-clay, and gum. Such a resist may be printed on the cloth by one roller of a two or three colour machine, and the catechu mixture (page 145) by another roller, or if required, two or three shades of the brown may be applied by as many rollers. The action of both of these resist pastes is chiefly mechanical; but the sulphate of zinc also acts by precipitating the catechu in solution, and thus preventing its access to the fibre of the cloth.

The same resist may be employed for preventing the deposition of catechu on a coloured design previously applied in madder colours. The specimen No. 8, page 145, is an example of such a combination of the topical, madder, and resist styles. To produce this pattern, the cloth is treated as follows:

1. Print by the two-colour machine with strong red liquor for the red, and with a mixture of iron liquor with a little red liquor for the dark puce;
2. Age, dung, and wash in the usual manner;
3. Dye in the madder-beck;
4. Clear by branning, &c., and dry;
5. Cover all the figures thus produced with a resist paste of sulphate of zinc, pipe-clay, and gum;
6. Apply the catechu ground by a roughened roller, and age for a couple of days, previous to washing at the dash-wheel.

A red shade may be given to the catechu ground by impregnating the entire surface of the cloth with weak red liquor, by a roughened roller, at the same time as the strong red and puce mordants are applied. Two shades of brown are sometimes imparted by applying the weak red liquor to certain parts of the ground, as for instance in broad stripes, the intervening space having catechu only.

5. DISCHARGE STYLE.

The manner of producing a white or coloured pattern on a coloured ground by the topical application of a "discharger" to a cloth already mordanted or dyed, is applicable to both mineral and vegetable colouring matters. Like the resist paste in the preceding style, the discharger may act either on the colouring matter itself or on the mordant before the cloth is exposed to a dyeing liquid. Dischargers for mordants are generally acid mixtures quite similar to resists for mordants, but dischargers for colouring materials are obtained from different classes of chemical substances according to the nature of the colouring matter to be removed. The essential property required in a discharger is that of converting the substances on the cloth into colourless or soluble products, which may be removed from the cloth so as not to interfere with the subsequent application of a colouring material to the parts discharged.

1. *Dischargers for colouring matters.*—The materials used as dischargers for vegetable colouring principles are chlorine and chromic acid, the bleaching powers of which have before been alluded to (pages 22 and 23).

To effect the topical discharge of a vegetable colouring matter by means of chlorine, with the production of a white figure, the dyed cloth is printed on those parts which are to be discharged, with a thickened acid mixture, the composition of which is varied according to the fastness of the colour to be destroyed, and after being suspended to dry for a day or two, the cloth is drawn (by a pair of squeezing rollers) through a solution of chloride of lime not stronger than 8° Twaddell or 1·040. The calico should be extended on rollers while being drawn through the solution, and should not occupy more than two or three minutes in its passage. The solution of chloride of lime is usually contained in a rectangular cistern of wood lined with lead, of the following dimensions; six or eight feet long, three feet wide, and four or five feet deep. As soon as the goods are taken out of the solution of chloride of lime, they are put to soak in water; after which they are washed either at the dash-wheel or in the rinsing machine, and then dried.

The chemical reactions which take place in this process are by no means complicated. Chloride of lime does not of itself bleach Turkey red and some other fast colours immediately; so that a cloth dyed with such colours may remain for some minutes in contact with a solution of chloride of lime without any deterioration in colour. But the acid applied to certain parts of the cloth combines with the base of the chloride and liberates free chlorine, which exerts an instantaneous bleaching action on the vegetable colouring matter on those parts of the cloth. Almost the only colours to which chlorine can be thus applied as a discharger, are Turkey red and other madder colours and indigo, as the more delicate colours are easily discharged by chloride of lime alone.

A white discharger adapted for all madder colours except Turkey red may be made by dissolving four pounds of tartaric acid in a gallon of water, mixing this solution with a gallon of lime-juice of spec. grav. 44° or 48° Twad., and thickening the mixture with pipe-clay and gum.

The white discharger for Turkey red requires to be somewhat stronger than the above. It may be made by mixing four pounds of tartaric acid with a gallon of lime-juice at about 30° Twad., and after thickening with pipe-clay and gum, adding about a pound of concentrated sulphuric acid, or two pounds of bisulphate of potash.

In a particular style of work, the Turkey red is discharged by the direct topical application of chlorine, or rather of an aqueous solution of chlorine. It is in this way that the celebrated Bandana handkerchiefs, which have white figures on a dark ground, have been most successfully imitated by Messrs. Monteith of Glasgow. The style is only practised in the manufacture of handkerchiefs.

From ten to fourteen pieces of cloth, previously dyed Turkey red, are stretched over each other quite parallel, and passed together by portions at a time (proceeding from one end of the pieces to the other end), between two leaden plates, one of which is superimposed immediately over the other. Each of these leaden plates is cut completely through so as to leave hollow places on all the parts required in white on the red ground. By means of a hydraulic press, the pieces of cloth are compressed between the leaden plates with a force of three hundred and twenty tons on the whole surface. While the cloth is exposed to this immense pressure, an aqueous solution of chlorine (obtained by adding sulphuric acid to a solution of chloride of lime) is made to percolate downwards through the pieces by the openings in the leaden plates. As the compressed state of the cloth prevents the imbibition of the liquid except by the parts opposed to the design on the lead, the solution passes on in a circumscribed channel to the lower leaden plate, where it escapes and is conveyed away by a waste-pipe. The portions of cloth through which the liquid passes are entirely deprived of their colour.

As soon as the chlorine solution is passed through, water is made to percolate in a similar manner to wash away the chlorine, else the definition of the pattern would be impaired. The passage through the cloth of the chlorine solution and the water for washing is sometimes assisted by a pneumatic apparatus consisting of a large gasometer, from which a current of air is caused to proceed under a moderate pressure, and act in the direction of the liquid.

When a considerable quantity of water has passed through the cloths, the pressure is removed and the pieces are washed and slightly bleached, whereby the lustre both of the design and ground is considerably increased.*

After the production of a white figure on a coloured ground by the application of the acid discharger and immersion in the solution of chloride of lime, coloured figures may be applied either to

* A detailed account of this interesting process, by Dr. Ure, may be found in the Journal of the Royal Institution for 1823.

the ground or to the white figure by grounding in topical colours by the hand-block. A common method of imparting a coloured figure is by mixing with the acid discharger one of the two solutions necessary for producing a mineral colouring material. For example, to impart a yellow figure to a piece of cotton dyed with Turkey red, such as the specimen No. 21, the cloth is treated in the following manner:

No. 21.

1. It is printed by the machine with a chrome-yellow discharger composed of

> 1 gallon of lime-juice of spec. grav. 20° Twad.,
> 5 pounds of tartaric acid,
> 4 pounds of nitrate of lead, with a mixture of
> pipe-clay and gum as the thickener.

2. After hanging for a day or two, the piece is passed through the solution of chloride of lime at 8° Twad.

3. It is soaked in water and then slightly winced in water.

4. The piece is next winced for about a quarter of an hour in a solution of bichromate of potash containing from three to five pounds to the piece.

5. It is lastly passed through, or winced in, dilute muriatic acid, washed at the dash-wheel and dried.

To obtain both a white and a yellow figure on a Turkey red ground, the dyed cloth may be printed with two acid dischargers, one intended for the production of the white figure, the other for the yellow figure. The subsequent treatment of the cloth is the same as above.

To impart a blue figure to the same ground, the dyed cloth is printed with a mixture of soluble Prussian blue, permuriate of tin, and tartaric acid, after which it is drawn through a solution of chloride of lime. The Turkey red thereby becomes discharged and the Prussian blue fixed on all the parts where the above mixture had been printed.

The only substance besides chlorine which can be conveniently employed to effect the topical destruction or removal of a vegetable colouring matter is chromic acid, which produces the decomposition of the colouring matter by virtue of its oxidizing power, the chromic acid becoming reduced to the state of green oxide of chromium. The vegetable colouring principle best adapted to this kind of work is indigo.

To obtain a white pattern on an indigo ground by means of chromic acid, the cloth is first dyed uniformly with indigo in the ordinary manner, and then padded with a solution of bichromate of potash containing about five or six ounces per piece. After being carefully dried in the shade at the ordinary temperature, the cloth is next printed with a discharger containing tartaric acid, oxalic acid, citric acid, and sometimes muriatic acid; and immediately after the impression it is winced in water containing some chalk in suspension, then washed at the dash-wheel, passed through dilute sulphuric acid, and lastly washed in clean water.

The colour of the indigo on the cloth is destroyed immediately on the application of the acid discharger: chromic acid is then liberated from the bichromate through the superior affinity of the acids in the paste for the potash, and the free chromic acid at once oxidizes and destroys the colouring matter. Indigo is almost the only substance which can be adapted to the chromic acid discharger, owing to the oxidizing action which the bichromate of itself exerts on vegetable colouring materials in general; hence the reason also for drying the dyed goods, after being padded with the bichromate, in a darkened chamber and at the ordinary temperature.

To produce a yellow instead of a white figure, the acid discharger may be mixed with a salt of lead: in other respects the process is the same as above.

The following method of obtaining a white figure on a dark green ground is an example of the combination of the madder style of work with the chromic acid discharge style.

1. Dip the cloth in the blue-vat to the desired shade;

2. Pad in a mixture of red liquor with bichromate of potash containing five or six ounces of the latter to the gallon, and dry in the shade;

3. Print the cloth, without being washed, with a mixture of lime-juice, sulphuric acid, and oxalic acid;

4. Pass the cloth through a mixture of hot water and chalk, and dye in a decoction of quercitron bark;

5. Wash and clear by branning.

In this process, the mixture of lime-juice, sulphuric acid, and oxalic acid, not only liberates chromic acid from the bichromate of potash, but also dissolves the subsulphate of alumina deposited from the red liquor: the parts on which this mixture is applied do not therefore become permanently dyed yellow when the cloth is exposed to the decoction of quercitron.

The discharge style is applicable to cloths dyed with mineral as well as with vegetable and animal colouring matters.

1. A white figure may be produced on a ground of Prussian blue, by imprinting on the cloth a paste containing a caustic alkali (either potash or soda), and passing the cloth afterwards through a solution of oxalic acid. The Prussian blue is here decomposed by the action of the alkali, affording yellow prussiate of potash, or prussiate of soda, which may be removed by washing, and peroxide of iron, which is precipitated on the cloth, but is afterwards dissolved out by the oxalic acid.

2. A white figure on a ground of manganese brown may be very readily obtained by imprinting the cloth, after being dyed brown in the ordinary manner (see page 174), with a slightly acid solution of protochloride of tin of a specific gravity about 70° or 80° Twad., or containing a pound and a half or two pounds of the protochloride per gallon, according to the intensity of the shade of the manganese ground. The solution of protochloride of tin is thickened with about a pound of starch to the gallon. The peroxide of manganese on the cloth is decomposed by the protochloride of tin and converted into protochloride of manganese, which being a very soluble salt is easily dissolved out by washing, leaving the parts white, or nearly so, on which the salt of tin had been applied. Peroxide of tin is formed at the same time, and remains for the most part attached to the cloth, but being white, it does not vitiate the pattern, and if required, may be made subservient to the application of the colouring principle of a vegetable dye-stuff, as peach-wood, quercitron, or logwood. As most acidulous mordants are capable of removing the peroxide of manganese and inserting their own bases instead, a great variety of coloured designs may be applied to the manganese ground by afterwards dyeing such goods in various dye-becks.

To impart a design in white, blue, and yellow on the bronze ground (such as the specimen No. 15, page 174), the cloth on which the manganese has been raised may be printed with the salts of tin for the white; with a mixture of berry liquor, alum, and salts of tin for the yellow; and with a mixture of salts of tin, prussiate of potash, pernitrate of iron, muriatic acid, and British gum, for the blue spots. The colour of the latter mixture is at first greenish-white, but it changes to blue on exposure to the air.

A design in different shades of red and pink may be communicated to the same ground by means of a mixture of peachwood liquor or cochineal liquor with alum, perchloride of tin, and protochloride of tin, thickened with gum tragacanth; and a mixture of logwood liquor, with alum and the two chlorides of tin, thickened with starch, may be used for imparting different shades of purple and violet to the same ground.

A figure in chrome-yellow may be produced on a ground of manganese bronze by printing on the dyed cloth a discharging material composed of tartaric acid, nitrate of lead, and salts of tin. After the cloth is dried, it is passed, first, through lime-water, then through a solution of bichromate of potash, and afterwards through dilute muriatic acid to brighten the yellow.

3. Protochloride of tin, when mixed with sulphuric and tartaric or oxalic acid, is also used as the discharging material for chrome-yellow and chrome-orange. The discharge of the chromates of lead is effected, in this case, by the reduction of the chromic acid to the state of green oxide of chromium, which forms soluble salts with the acids.

A variety of coloured designs may also be applied by combining with the discharger, the materials for the production of a topical colour. Thus, a blue figure is sometimes produced by printing on the orange or yellow cloth a mixture of the two chlorides of tin, Prussian blue, and muriatic acid; a violet figure, by logwood liquor mixed with alum, tartaric acid, protochloride of tin and starch; and a red or pink figure, by a similar mixture containing peach-wood liquor instead of logwood liquor.

Another material which may be used for discharging chrome-yellow and chrome-orange, with a view of producing a white figure, is a strong caustic alkaline solution, but protochloride of tin will generally be found more convenient and more effective.

4. A white figure on a ground of iron buff (page 172) is obtained by applying to the coloured cloth a mixture of tartaric and oxalic acids with lime-juice, thickened with pipe-clay or China-clay and gum. The acids dissolve the peroxide of iron, and the figure is obtained perfectly white by washing. The readiest way of discharging the iron is to apply the acid mixture after the cloth has been padded in the iron liquor, and before it is exposed to the alkaline solution to precipitate the peroxide. A solution of protochloride of tin in a dilute acid, thickened with starch, is also sometimes used as a white discharger for iron buff; and for producing coloured designs the protochloride may be mixed with perchloride of tin and either logwood liquor, peachwood liquor, or berry liquor.

The following method of producing white and buff-coloured figures on a dark green ground is an example of the combination of such a process as the above with the resist style.

1. The cloth is printed with the white resist for the indigo-vat (No. 2, page 187);

2. It is dipped into the blue-vat, rinsed, and dried;

3. It is padded with rather weak iron liquor and aged;

4. A solution of tartaric and oxalic acids in lime-juice, thickened with pipe-clay and gum, is applied by the block to parts of the buff spots;

5. The cloth is washed in water holding chalk in suspension to remove the acid paste;

6. It is lastly winced in an alkaline solution, to raise the buff, and then washed.

The white figure is here produced by the discharge of the salt of iron from parts of the spots on which the indigo had been resisted; the buff figure is the remainder of those spots, and the dark green ground results from the mixture of the indigo with the buff.

2. *Dischargers for mordants.*—Another method of producing white or coloured figures on a coloured ground, referable to the discharge style of work, is by the removal of the mordant previous to the application of the colouring material. This method is particularly adapted to grounds of madder and logwood with an iron or aluminous mordant. The material used for the discharge of the mordant is usually a mixture of tartaric acid, oxalic acid, and lime-juice, the proportions of the constituents being varied according to the strength of the mordant to be discharged. The following mixture may be

used for discharging the mordant from a piece of cloth impregnated with red liquor of spec. grav. 7° Twad. or weaker, or with iron liquor of spec. grav. 2° Twad. or weaker:

1 gallon of lime-juice of spec. grav. 6° Twad.,
3½ ounces of oxalic acid, and
4 ounces of tartaric acid,
Thickened with pipe-clay and gum if for application by the block, or with British gum if by the roller.

Sometimes the proportion of tartaric and oxalic acids and the strength of the lime-juice are considerably reduced, and bisulphate of potash, oil of vitriol, and cream of tartar are introduced instead.

The ordinary operations practised on calico in this style of work to obtain a white figure are the following:

1. The cloth is padded or printed with the solution of the mordant for the ground, and is immediately dried by being drawn either through the hot-flue or over steam boxes;

2. After a moderate ageing, the calico, without being washed, is imprinted by the roller with the discharging paste, which immediately dissolves the subsalt formed during the ageing;

3. The calico is next suspended for a day or two in a cool place, not very dry, and if the mordant is peroxide of iron, it is then passed through water heated to about 130° Fahr. and rendered slightly alkaline by the addition of a small quantity of carbonate of soda;*

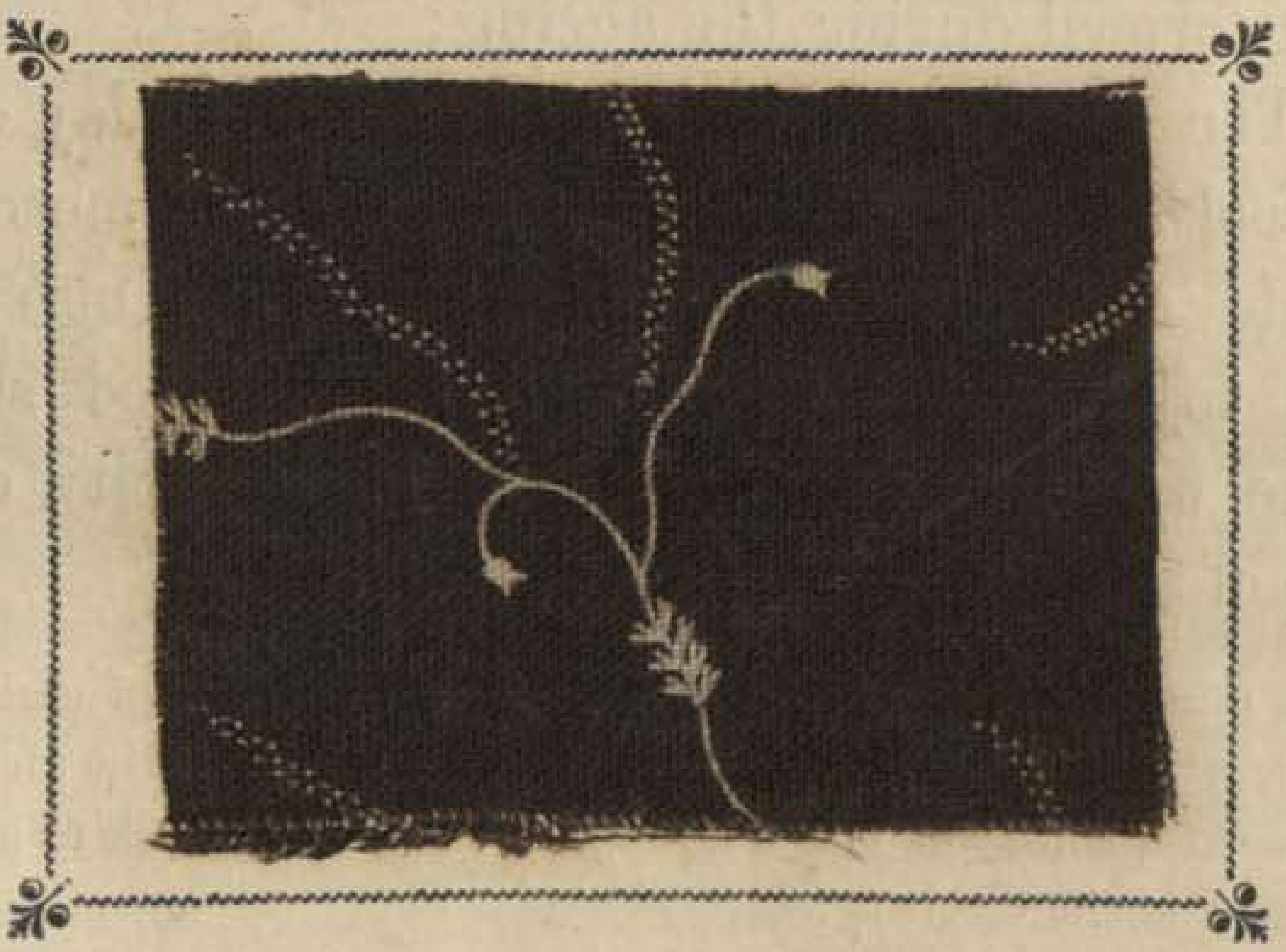
* The passing of the cloth through a dilute solution of carbonate of soda is sometimes omitted, particularly when alumina is the mordant, in which case a quantity of chalk is added to the dung-beck to neutralize the free acid in the discharger.

4. The cloth is afterwards washed, dunged, and dyed in the vegetable infusion; after which it is cleared by soaping or branning and wincing in solution of chloride of lime in the usual manner. Wherever the acid paste had been applied, the colouring material does not attach itself, in consequence of the removal of the mordant from those parts.

It will be observed that this kind of discharge work is very similar to the resist style, in which an acid paste is first imprinted on the cloth to prevent the attachment of a mordant subsequently applied to the whole surface of the cloth (see page 179); the only difference between the two styles consisting in the order of applying the acid and the mordant. The best whites are no doubt generally procured by the resist style; as it is easier for an acid to prevent the attachment of a mordant in an insoluble form, than to dissolve it, when once precipitated.

To procure a white design on a black ground, such as the annexed specimen (No. 22), by the discharge

No. 22.



of the mordant, the cloth may be treated in the following manner:

1. Pad or print the calico with a mixture of equal measures of iron liquor of spec. grav. 6° Twad., and red liquor of 8° Twad., thickened with starch or British gum;

2. Dry over the steam boxes, age, and apply a discharger composed of tartaric acid, sulphuric acid, and lime-juice, thickened with British gum;

3. Pass the cloth through warm water mixed with chalk;

4. Dye in decoction of logwood, mixed with a little bran and dung;

5. Wash, clear the white by branning, rinse and dry.

The following method of producing white and blue figures on a purple or chocolate ground presents an example of the combination of such a style as the above with the indigo resist style:

1. The white calico is padded with red liquor;

2. After the cloth has been aged for a short time, the thickened acid discharger is applied by the cylinder to all the parts intended to be blue or white;

3. After hanging for twenty-four hours, the calico is dunged, dyed in the madder-beck, and cleared by branning;

4. On the parts of the white spots which are intended to remain white, the sulphate of zinc resist for the indigo-vat, such as the mixture described at page 187, is imprinted;

5. After the cloth is dried, it is dipped into the

blue-vat and exposed to the air; then washed at the dash-wheel, and dried.

The white figure is here produced through the discharge of the aluminous mordant by the acid, and by the action of the sulphate of zinc resist on the indigo: the blue figure is produced by the indigo on the white spots to which the resist was not applied, and the purple or chocolate ground results from the mixture of the indigo with the madder red.*

A discharger for one mordant is sometimes mixed with the solution of another mordant on which it exerts no action, so that the mordant in the discharger becomes attached to the cloth, on the spots from which the previous mordant is removed. Thus, subacetate of iron may be separated from a piece of calico, and alumina imparted in its place by applying to the mordanted cloth a mixture of red liquor with protochloride of tin. In this manner, a red figure on a violet or lilac ground is sometimes produced, the cloth being first covered with weak iron liquor, then dried, printed with the mixture of red liquor and protochloride of tin, dunged,

* A simpler and better method of obtaining the same effect is by the "chocolate ground neutral style," the principle of which is described at page 194. The cloth is first printed with the white cupreous resist (mixed with a free acid, when a very well defined figure is required), and afterwards with the chocolate resist (page 195) for the ground, the parts required in blue being left white. The cloth is then aged, drawn once through the blue-vat, washed, dunged, dyed with madder, and cleared by branning. This interesting style of work is very little practised at present, it being superseded by the cheaper but much less permanent steam blue and steam sapan chocolate, of which a specimen is introduced at page 158.

dyed in the madder-beck, and cleared in the usual manner. To obtain a white figure as well as the red, the mordanted cloth should be also printed with lemon-juice, or with a mixture of lemon-juice and sulphuric acid.

The use of a mixture of protochloride of tin and red liquor as a red *resist* for iron liquor, with the view of producing the same effect, has before been adverted to (pp. 181, 182). One of these two processes is almost always followed whenever a figure in madder red is required on a ground of madder purple or black.

In a few ingenious processes related to this kind of work, for producing coloured figures on coloured grounds, an acid solution of protochloride of tin is applied as a kind of discharger to a cloth dyed uniformly with peachwood, quercitron or madder, by means of an iron mordant.

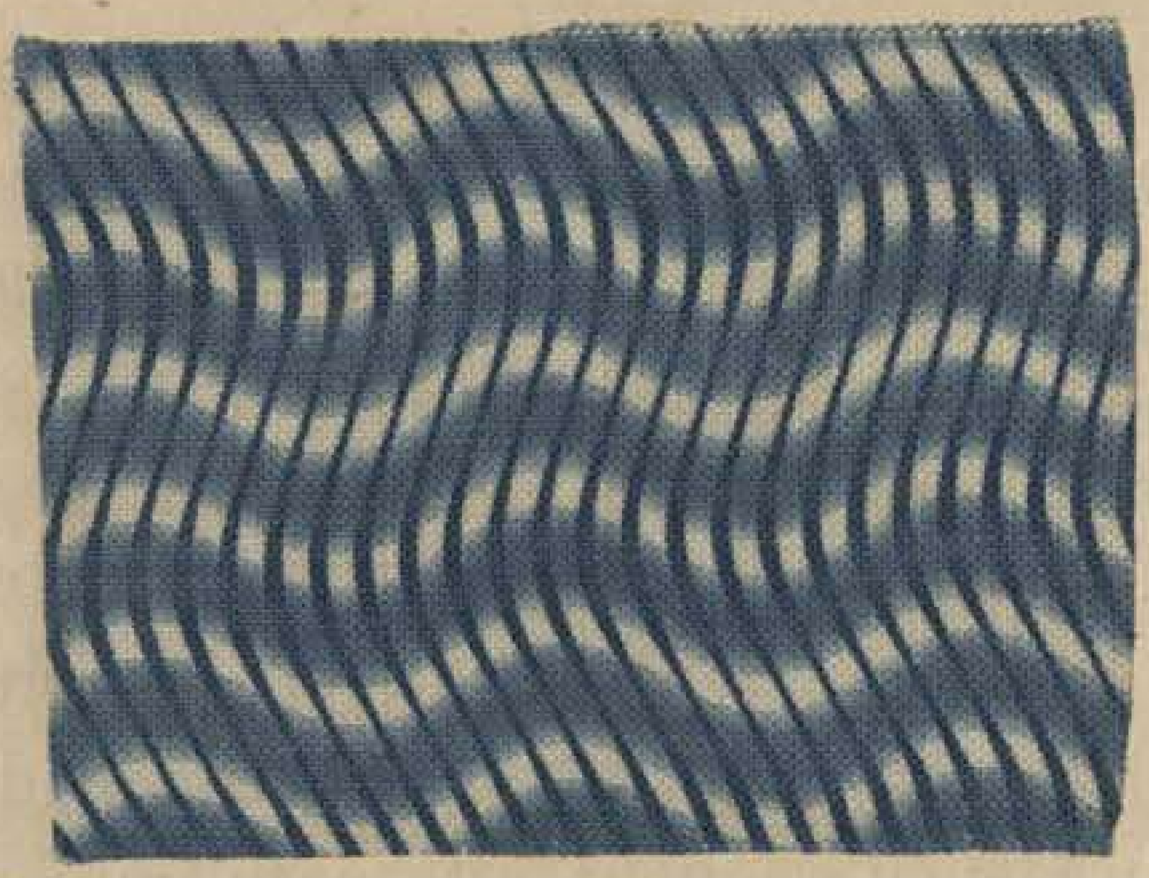
By mutual decomposition, the protochloride of tin in the discharger and the peroxide of iron on the cloth give rise to chloride of iron and peroxide of tin, or rather, the oxide of tin intermediate between the protoxide and peroxide. The chloride of iron, being soluble, is removed by washing, but the insoluble oxide of tin remains attached to the fibre, and combines with the colouring principle previously united to the oxide of iron. This double decomposition of oxide of iron and protochloride of tin may be made subservient to the production of a red figure on a black ground. For this purpose the cloth is first covered with iron liquor, then dyed to a black in decoction of peachwood, and afterwards printed with the acid solution of the protochloride. Wherever the salt of tin is applied, the colour of the cloth changes from black to red, through the transference of the colouring principle of the peachwood from oxide of iron to oxide of tin. In a similar manner, a red figure may be obtained on a ground of madder purple or lilac, and by substituting quercitron for madder or peachwood, a yellow figure is produced on a drab ground. The iron liquor employed in these processes should not be stronger than 3° or 4° Twad.

6. CHINA BLUE STYLE.

The style of calico-printing by which the China-blue prints are produced is an interesting modification of the topical style. These prints are distinguished by having blue figures, usually of two or three different depths of colour, associated with white, as the specimen No. 23.

To produce such a pattern, the bleached calico is subjected to the following operations. It is first printed, either by the block or cylinder, with a mixture of indigo, orpiment (sulphuret of arsenic), sulphate of iron or iron liquor, gum or starch, and water; the proportions of gum or starch and water being varied according to the depth of colour required. After being printed, the calico is suspended in a dry atmosphere for a day or two, and stretched in perpendicular folds on a rectangular wooden frame suspended by pulleys and a rope from the ceiling of the apartment. The frame with the cloth is then dipped

No. 23.



in a certain order into the three following liquids: No. 1, milk of lime; No. 2, solution of copperas; No. 3, solution of caustic soda. These liquids are contained in three adjacent stone cisterns, the tops of which are on a level with the ground: the usual dimensions of the cisterns are, eight or nine feet in length, four feet in depth, and three feet in width.

Into the vats No. 1 and No. 2, the calico is dipped several times alternately, with exposure to the air for a short time between each dip; it is not dipped so frequently into the vat No. 3, and the dipping in this always immediately follows No. 2. By these operations, the insoluble indigo-blue applied to the surface of the cloth becomes converted into indigotin which is dissolved and transferred to the interior of the fibres, where it is precipitated in the original insoluble form.

The chemical changes which take place in these successive operations are rather complicated, but admit, nevertheless, of a satisfactory explanation. By the successive immersions in milk of lime and solution of sulphate of iron, protoxide of iron comes to be precipitated on the surface of the cloth. This protoxide of iron, with the assistance of the lime, reacts on the indigo imprinted on the calico, converting it, through the intervention of water, into indigotin, which dissolves in the lime-water, and the solution is absorbed into the pores of the cloth. On exposure to the air, the indigotin absorbs oxygen, and insoluble indigo-blue is deposited within the fibre in a fixed state. The protoxide of iron produced in the subsequent alternate immersions into the sulphate of iron vat and into the lime-vat, acts only on the indigo which still remains on the surface of the calico, not having free access to the indigo within the fibre; and as the alternate dippings are continued (up to a certain number), so the proportion of indigo on the surface diminishes, and that of the indigo within the fibre increases.

The orpiment contained in the pigment printed on the cloth seems to act chiefly by increasing the density of the mixture, thus preventing its ready disintegration and removal by the various liquids to which the cloth is exposed. It also assists, probably, in deoxidizing the indigo-blue in conjunction with the lime.

By these operations the whole surface of the cloth becomes impregnated with a considerable quantity of oxide of iron, to remove which, the cloth is plunged (being still on the frame) into a fourth similar cistern containing sulphuric acid of about the spec. grav. 5° Twad. (1·025.) It is afterwards washed in clean water, and then again brightened in dilute sulphuric acid. Lastly, the clearing of the white ground is sometimes completed by exposing the cloth to warm soap-water.

The following method of preparing the China blue mixture of different shades is described by M. Thillaye, in his useful work on calico-printing.* The materials employed are,

15¾ pounds of indigo, in coarse powder,
3¾ pounds of orpiment,
22 pounds of copperas, and
9½ gallons of water, or water and gum-water.

The indigo, orpiment, copperas, and four gallons and a half of the water are well ground together in a mill for three days; the mass is then removed, and the mill is washed with a gallon of water which is added to the mixture. The remaining four gallons of water are afterwards added; but if a very thick blue is required, as much strong gum-water is introduced instead. From this mixture, which may be called No. 1, several lighter shades are procured by diluting it with water or gum-water in the following order:

No.	Quantity by measure of No. 1.		Quantity by measure of water or gum-water.
1	1	mixed with	0
2	11	"	1
3	10	"	2
4	8	"	4
5	6	"	6
6	4	"	8
7	2	"	10
8	2	"	12
9	2	"	14
10	2	"	16
11	2	"	18
12	2	"	20

* *Manuel du fabricant d' Indiennes*, Paris, 1834.

To produce a small single blue figure, the mixture No. 5, thickened with starch, may be applied by the block, and No. 4, thickened with gum, by the roller.

For two different blues, applied by the block, there may be used, 1°, the mixture No. 4, thickened with starch; amd 2°, N. 9, thickened with gum.

For three different blues, applied by the block, there may be taken, 1°, the mixture No. 5, thickened with starch; 2°, No. 7, thickened with starch; and 3°, No. 10, thickened with gum.

The mixture described by M. Thillaye is not exactly the same as that commonly employed in this country. Instead of copperas, the Lancashire printers generally use iron liquor, and British gum instead of common gum; they also take little more than half as much orpiment as is directed in the receipt of M. Thillaye. The following proportions of the materials will probably be found to form a convenient mixture:

16 pounds of ground indigo,
5 or 6 gallons of strong iron liquor,
2 pounds of orpiment, and
British gum and water sufficient to make 8 gallons.

When required for use, this mixture, which contains two pounds of indigo to the gallon, may be diluted with water or gum-water in the order following:

No.	Quantity by measure of above mixture.	Quantity by measure of water or gum-water.	Quantity of indigo in one gallon of the mixture. lbs.	oz.
1	1	0	2	0
2	1	½	1	5¼
3	1	¾	1	3¼
4	1	1	1	0
5	1	2	0	10¾
6	1	3	0	8
7	1	5	0	5¼
8	1	7	0	4
9	1	9	0	3⅕
10	1	12	0	2½
11	1	16	0	1¼

The darkest of the two shades of blue in the specimen of this style of printing (page 215) was produced from a mixture containing one pound of indigo to the gallon (as No. 4), and the lighter from a mixture containing three ounces of indigo to the gallon (No. 9). Both were thickened with two pounds of British gum per gallon, and were applied at once by the two-colour machine.

The milk of lime for dipping China blue prints may be prepared by mixing two hundred pounds of lime with a thousand gallons of water. When in constant use, the lime-vat requires to be replenished twice daily, both with lime and water.

The strength of the solution of copperas is varied from 3½° Twad. (1·017) to 6° Twad. (1·030), it being regulated more by the quantity of the figure in the pattern than by the depth of colour required. The kind of copperas generally preferred for this purpose is that technically known as "green copperas," which contains a small quantity of free sulphuric acid. The superiority of this variety of copperas merely consists in the comparative slowness with which it becomes peroxidized or "rusty" by exposure to the air. The copperas-vat does not require replenishing quite so frequently as the lime-vat, and the cistern need not be emptied for six months or longer. The bottom and sides of the cistern become lined with a dense crystalline deposit of oxide of iron and sulphate of lime, as hard as the cistern itself.

The strength of the solution of caustic soda may vary from 6° to 9° Twaddell (1·030 to 1·045). It is made in the usual manner by carbonate of soda and quick-lime.

The order of dipping the frame into the three cisterns is as follows:

1. Dip in the first vat (lime) for ten minutes.
   Drain for five minutes.
2. Dip in the second vat (copperas) for ten minutes.
   Drain for five minutes.
3. Dip in the first vat for ten minutes.
   Drain for five minutes.
4. Dip in the second vat for ten minutes.
   Drain for five minutes.
5. Dip in the third vat (soda) for ten minutes.
   Drain for five minutes.
6. Dip in the second vat for ten minutes.
   Drain for five minutes.
7. Dip in the first vat for ten minutes.
   Drain for five minutes.
8. Dip in the second vat for ten minutes.
   Drain for five minutes.

9. Dip in the first vat for ten minutes.
   Drain for five minutes.
10. Dip in the second vat for ten minutes.
   Drain for five minutes.
11. Dip in the third vat for ten minutes.
   Drain for five minutes.

The addition of a small quantity of nitrate of lead to the China blue mixture, when iron liquor and not copperas is used, is said to impart considerable vivacity to the colour; but I am not aware of its being usual to make this addition, unless with a view of producing a green instead of a blue design, when the cloth, after having been dipped as above and cleared in dilute sulphuric acid, is winced in a solution of bichromate of potash in order to produce chrome-yellow. This is by no means an advantageous process for obtaining a green figure in the China blue style, as the lime and soda vats are apt to become so highly charged with oxide of lead as to deposit that oxide on the white parts, which consequently become yellow when the cloth is exposed to the bichromate. A better method is to add red liquor and perchloride of tin to the China blue mixture, and to dip in the three vats in the usual manner; after which the cloth is cleared in very dilute sulphuric acid, dyed in decoction of quercitron mixed with size, cleared by branning, and lastly, winced in a dilute solution of alum to brighten the green.

Printing of mousselin de laines, silks, chalis, &c.—The fixation of colouring matters on fabrics of silk and wool is commonly effected by the process of steaming. No mineral colouring material, with the exception of Prussian blue, is applied to these tissues; nor is it usual to impart to them colouring matters from infusions of vegetable or animal productions by the madder style, except in a few difficult processes of silk printing. These fabrics were formerly printed entirely by the block, but latterly the roller and the press machine (page 125) have been substituted.

The colour mixtures for de laines, which are formed of cotton and wool, should be of such a nature as to afford an uniform deposit of colouring matter on both the animal and vegetable fibre. These mixtures are sometimes composed of two distinct bases, one capable of attaching itself firmly to the wool, the other to the cotton. Thus, a preparation sometimes used for imparting a blue colour to de laines, is a mixture of the steam blue for cotton (see page 158) with indigo-paste or soluble blue (sulph-indigotate of potash) for the wool. In a particular kind of fancy dyeing, the woollen thread only is dyed, and the cotton is afterwards perfectly bleached by exposing the dyed de laines to a dilute solution of bleaching powder. The cotton thread is sometimes dyed of another colour, either before or after the dyeing of the woollen thread. Before being printed, de laines are always impregnated with peroxide of tin, from two different solutions applied consecutively as already described (see page 45). The steaming of the printed de laines, which is performed either by the column or chamber, usually lasts about three-quarters of an hour; but the time varies according to the quantity of acid in the mixtures, and to the manner in which the steam is applied. With a considerable quantity of acid, the fibres become weakened if the process is prolonged, and a shorter time is required with the column than with the chamber.

In general, the only difference between the composition of the mixtures for steam colours for woollen goods and those for cotton goods (page 152) is that the former contain more free acid than the latter, or that the colouring matter is held in solution more strongly in the former than in the latter. Whether the mordant is perchloride of tin, protochloride of tin, or alum, a considerable quantity of tartaric or oxalic acid is almost always introduced. The most vivid colours are generally obtained by protochloride of tin, with either oxalic or tartaric acid.

The brilliant steam blue distinguished when on woollen goods as "royal blue," is formed through the decomposition of hydroferrocyanic acid, as before explained. The composition of the mixture printed on the cloth is much the same as the steam blue for cotton (page 158), but is more concentrated, and perchloride of tin is introduced instead of alum. The solution of yellow prussiate of potash, which should contain not less than three pounds of the prussiate in a gallon, is mixed with sufficient tartaric acid to precipitate the whole of its potash as bitartrate of potash (cream of tartar), which may be separated and employed in the preparation of tartaric acid.

The best mixture for a steam scarlet for woollen goods, is made of cochineal liquor, gall liquor, protochloride of tin, and oxalic acid. It may be thickened with gum, if for blotches or grounds; and with starch, if for small figures. The best mordant for producing different shades of yellow with berry liquor is a mixture of alum and red liquor; and with decoction of quercitron bark, a mixture of red liquor and oxalic acid, or else alum alone.

The only preliminary operations to which silken cloth intended to be printed, is commonly subjected, are, 1°, boiling in a solution of soap and carbonate of soda to remove the "gum;" 2°, passing through dilute sulphuric acid; and 3°, washing and drying. Some printers recommend the steeping of the silk in a solution of alum, after it is taken out of sulphuric acid, but this is by no means a common practice. The processes for printing and dyeing silks according to the madder style, are very similar to those for cottons: the thickened mordant is first applied; the piece is then dried, aged for a couple of days, winced in bran-water, dyed in the hot vegetable decoction, and cleared by being winced in boiling bran-water. In some styles of work, the silk is afterwards soaped, impregnated with a solution of tin, and, lastly, passed through very dilute sulphuric acid.

The madder style of printing and dyeing is rather difficult of execution on silken cloth, and is consequently not much practised on this variety of textile fabrics. The common method of ornamenting silk with different coloured designs is by means of steam colours, a great variety of which may be imparted of sufficient fixity to bear all ordinary exposure to deteriorating influences. With the exception of the preliminary operations previous to the application of the colour-mixture, the treatment of silks in this style of work is the same as that of cottons.

A remarkable style of printing and dyeing is largely practised on silken and woollen goods, which possesses not the smallest resemblance to any one of the varied processes to which cotton goods are subjected. This is the *mandarining style*, by which a yellow or orange colour may be communicated to the silk or wool by exposing the stuff to the action of nitric acid. The colour proceeds from a peculiar substance formed through the decomposition by the acid of a portion of the fibre of the cloth itself. On the parts intended to be preserved white, the contact of the acid with the cloth is prevented by the application of a resist paste composed of resin and suet.

Taking, in the first place, the simplest illustration of this style of work, that is, the production of a white design on an orange ground, the operations practised on the cloth are the following.

The silk, having been first cleaned from its resinous coating in the usual manner, is printed on the parts which are to remain white with the fatty resist of resin and suet. A quantity of this mixture is kept in a melted state near at hand, and a portion is occasionally laid over a piece of woollen cloth stretched on a frame which forms the top of a copper chest. Steam is admitted into the chest by a pipe in order to preserve the resist in a liquid state. When the silk is ready to receive the resist, the printer heats his block, takes up some of the resist from the frame, and applies it immediately to the silk by a light blow with a mallet. The block is instantly removed, to prevent it from adhering to the silk.

When the printing of the whole piece is completed, the silk is passed through dilute nitric acid, obtained by adding from one to two parts of water to one part of aquafortis of commerce; the acid is heated as high as possible without endangering the solidity of the resist paste, the melting of which would evidently be attended with serious inconveniences. The silk should not remain in the acid longer than one minute.

The nitric acid is contained in a sand-stone or an earthenware trough, which is placed within a copper or wooden box to serve as a water-bath: the heat applied is that of steam. A reel is placed on each side of the trough to guide the silk as it enters and leaves the acid.

On being withdrawn from the acid, the silk is immediately washed in a stream of cold water; after which, the resist is cleared away, and the orange brightened by wincing the silk in boiling soap-water to which a little soda is added. The piece is lastly washed in cold and hot water successively, and dried.

Such is the method of obtaining a white figure on an orange ground. Coloured figures are obtained in this style of work by a variety of ingenious and elegant processes, applicable, like that just described, to chalis as well as silks. One or two examples will suffice as illustrations.

White and blue figures on an orange ground may be procured in the following manner. The piece is first printed with the resinous resist, to preserve the parts which are to remain white from contact with the acid. It is next dyed blue in the indigo-vat in the ordinary manner, washed and dried, and the resist is then printed on those parts which are to remain blue. The next process is the mandarining, or passing through the nitric acid; by which the indigo is destroyed on all parts of the cloth except where the resist is applied, the cloth thus acquiring a ground of orange. The piece is lastly washed, and the orange brightened by a boil in soap-water with a little alkali.

An orange ground having been applied to the cloth by such a process as the preceding, the colour of the ground may be afterwards modified or completely altered by dipping the cloth in some dyeing liquid, the figures being still protected, if necessary, by the resinous resist. For example, a design in white and blue figures on a green ground may be imparted to a chali by simply dipping the piece, after having been treated as above for blue and white figures on an orange ground, in the blue-vat, previous to the removal of the resinous resist from the blue and white figures. White, blue, and orange figures on a green ground may be obtained by imprinting the resinous resist on the silk or chali after the mandarining process, and before the second immersion in the blue-vat.

An orange figure on a blue ground is sometimes produced by printing the nitric acid thickened with British gum upon the cloth previously dyed in the blue-vat. The piece is afterwards exposed to the action of steam, and is lastly boiled in soap-water to brighten the orange.

Superficial as the preceding account of calico-printing processes may and must appear to those who are acquainted, both practically and theoretically, with all the details of this beautiful art, it will probably be found sufficiently minute and exact to substantiate the claim of calico-printing to be considered not only one of the most important, but the most ingenious and refined of all the chemical arts. From the great variety of processes and of materials employed, almost every principle in theoretical chemistry receives an application or illustration in some one or other of the operations of the calico-printer. It has thus happened that several interesting discoveries in theoretical chemistry, made in the experimental laboratory, have actually been anticipated by the printer, from observations made in the print-works and dye-house.

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