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# APPLIED CHEMISTRY;

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IN

## MANUFACTURES, ARTS, AND DOMESTIC ECONOMY.

EDITED BY

**EDWARD ANDREW PARNELL,**

Author of "Elements of Chemical Analysis," late Assistant Chemical Lecturer  
in the Medical School of St. Thomas's Hospital.

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ELEMENTARY INSTRUCTION  
IN  
CHEMICAL ANALYSIS:

BY  
DR. C. REMIGIUS FRESENIUS,  
*Chemical Assistant in the Laboratory of the University of Giessen;*

WITH A PREFACE,

BY  
PROFESSOR LIEBIG.

EDITED BY  
J. LLOYD BULLOCK,  
*Member of the Chemical Society.*

☞ This Introduction to Practical Chemistry is admitted to be the most valuable Elementary Instructor in Chemical Analysis for scientific operatives, and for pharmaceutical chemists, which has ever been presented to the public.

The volume comprises two parts; of which the following analysis will convey an adequate and correct view:

**PART I.—INTRODUCTORY COURSE OF QUALITATIVE CHEMICAL ANALYSIS.**—The Preliminary Remarks unfold the definition, design, and utility of this analysis. It is divided into three chapters. Chapter I. delineates the operations, apparatus and utensils used in chemical analysis.—Chapter II. describes the “Reagents,” in two generic classes. 1. Reagents in *the humid way*—distinguished as simple, or chemical solvents, or which separate or characterize groups of substances; and special Reagents, which detect or separate individual bases, or are applied for those purposes to acids. Under those several heads are enumerated sixty different Reagents.—2. Reagents in *the dry way*—comprising “fluxes and means of decomposition; and blow-pipe Reagents,” including nine different substances.—Chapter III. exhibits the relation of the various substances to reagents; particularizing the metallic oxides, in six groups—the relation of *inorganic* acids to reagents, in three groups; and of *organic* acids, in three groups; the whole combining fifty-four substances.

**PART II.** develops a **SYSTEMATIC COURSE OF QUALITATIVE ANALYSIS.** The first chapter displays the Practical Process in several sections. 1. The preliminary examination of a solid body, a metal, with or without alloy, or a fluid.—2. Solution of bodies or classification of substances.—3. The real examination of compounds—substances soluble in water—substances insoluble in water, but soluble in acids, or aqua-regia substances insoluble, or sparingly soluble both in water and acids. This practical process illustrates the various substances previously enumerated; with the rules necessary for the perfection of the analysis.—4. Those descriptions are followed by “Confirmatory Experiments.” The second chapter includes Explanatory Notes, and Additions to the Practical Course.—To which is subjoined an Appendix, comprising an arrangement of the succession in which the chemical substances should be analyzed—and a classified Table of the forms and combinations of the substances enumerated.

*Extract from Editor's Preface.*

This work has already gone through two editions in Germany. The abundant opportunities enjoyed by its author of discovering the wants felt by students in entering upon the practice of Chemical Analysis, and his position in the school at Giessen, has enabled him to devise a method of study of the highest value. That it has received the approbation of the illustrious head of that school, and the benefit of three years' practical experience, under his immediate observation, must powerfully recommend it to the English student of Chemistry. Whoever is desirous of obtaining the knowledge necessary to become a practical chemist, will be in no small way indebted to Dr. Fresenius for the facilities thus afforded him. The Author in his preface tells us that he was led to compose this volume upon perceiving that the larger works on Chemical Analysis, such as H. Rose's, Duflo's, and others, although admirable in themselves, present great difficulties to beginners; which difficulties may be summed up under three heads: 1st. Too great copiousness and detail; 2nd. The absence of explanation of the Cause of Phenomena, i. e. the *theory* of the operations and reactions: and, 3rd. The omission altogether of many substances of very frequent occurrence, especially in the operations of the Pharmaceutist; such as the organic acids, &c. In avoiding these objections to former works on Chemical Analysis, Dr. Fresenius I think is not chargeable with having fallen into the opposite extreme of being too concise or elementary.

For my own part I may be allowed to observe that the English edition was undertaken by the express desire of Professor Liebig, who kindly recommended its being entrusted to my care. The author has furnished me with many corrections and some additions, and the hope is shared by us in common that it will facilitate the study of Analytical Chemistry to the student, and in every way serve to promote the interests of the Science.

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IN

## MANUFACTURES, ARTS, AND DOMESTIC ECONOMY.

EDITED BY

EDWARD ANDREW PARNELL,

AUTHOR OF "ELEMENTS OF CHEMICAL ANALYSIS," LATE ASSISTANT CHEMICAL LECTURER  
IN THE MEDICAL SCHOOL OF ST. THOMAS'S HOSPITAL, ETC.

- I. PRELIMINARY OBSERVATIONS.
- II. GAS ILLUMINATION.
- III. PRESERVATION OF WOOD.
- IV. DYEING AND CALICO-PRINTING.

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## P R E F A C E .

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THE "Preliminary Observations," with which this volume commences, comprise some brief considerations on the fundamental doctrines of chemistry, most of which may be included in an account of the general laws which govern, and the phenomena and changes which accompany, the chemical combination of different bodies. This introduction concludes with an explanation of Chemical Symbols, and a table of Equivalents.

The article on Gas Illumination comprises not only a detailed account of the process of making light-gas from coal, and of the chemical and physical properties of the constituents of coal-gas, but several important collateral subjects; among which are some considerations on the modes of burning gas and on the economy of gas illumination, descriptions of the process for making light-gas from other sources than coal, and an account of the applications which the secondary products of the coal-gas manufacture have received. The construction of different kinds of regulators and meters, and the process of "naphthalizing" gas, are also considered.

In the article on the Preservation of Wood, which follows that on Gas Illumination, means are pointed out for effectually guarding against the ordinary decomposing influences of air and water on timber. A considerable portion of the article is devoted to an account of the important experiments of Mr. W. Hyett, on the effects of the impregnation of wood with foreign substances.

Dyeing and Calico-printing forms the comprehensive subject of the concluding article of the present volume. Most of the leading processes now practised by the calico-printers of this country are there described, accompanied with explanations of the scientific principles on which they are based. Several of these processes, new to treatises on the subject, will be found of considerable value.

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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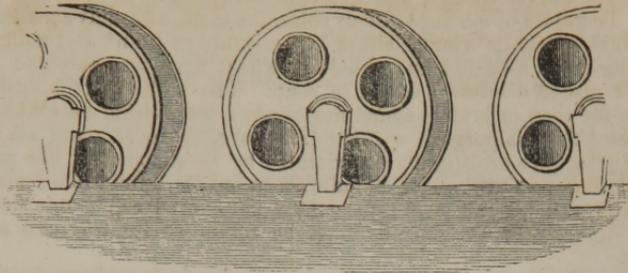
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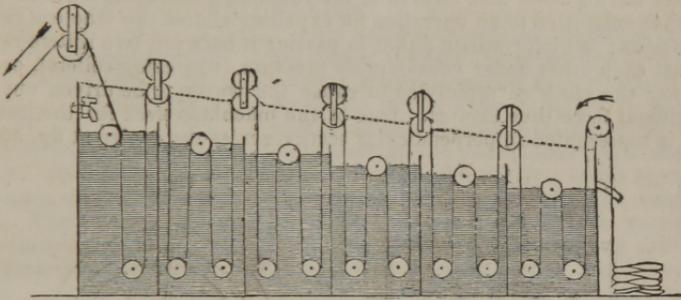
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Fig. 33.



In the washing of cloths which require delicate treatment, as those dyed with fancy or spirit colors, 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 ten compartments, by partitions which gradually decrease

Fig 34.



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 coloring 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 color, the cloth, after having been washed at the dash-wheel, is winced either in a mixture of bran\* and boiling water, containing about 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 teints of all vegetable coloring principles are slightly deteriorated by these agents. For most vegetable coloring matters besides madder, bran only is admissible; and even in bran-water, the wincing sometimes must not exceed a few minutes. With madder colors only, the wincing may be continued for from ten to twenty minutes.

The complete removal of the superfluous color from a piece of cloth which is to present a white pattern is generally effected, when madder is the only vegetable coloring 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 coloring 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, sometime 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 color, 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

Fig. 35.

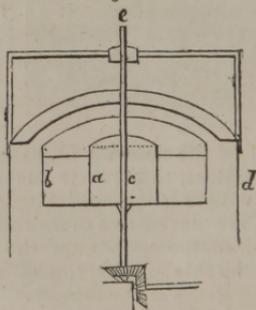
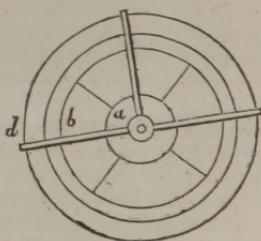


Fig. 36.



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, 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, whence it

\* In effecting the removal of this excess of coloring matter, the most active constituent of the bran seems to be the husky part. The feebly combined coloring 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*.

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 129).

When the cloth has been thus far dried, either by the squeezers or the "water extractor" just described, it is folded evenly and then passed, in the length of ten pieces, through a mixture of blue starch and water. A cross section of the

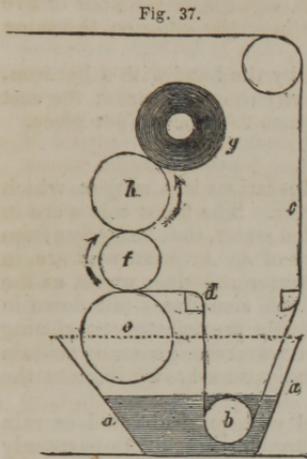


Fig. 37.

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.

After being starched, the ten pieces of calico are 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 circumference 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 arrow in the above figure. The drums are surmounted by a hood and flue for the purpose of conducting the stream 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

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

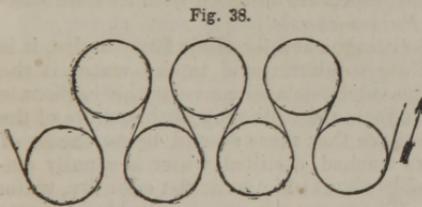


Fig. 38.

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 calicoes 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 colors 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 fall down in combination with the coloring 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 color, and imparts only a faint red color 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 color. In the first case, the quantity of madder red remaining 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 color, 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 Fernambouwood 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 colors of the dyed or printed goods. It is of importance that there should be no excess of the acid. When cochineal colors are washed, distilled water is usually employed; but where this can not 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. Clarke'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 colors. Not only is the shade of color modified by the attachment of the organic matter, but certain metallic coloring 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 coloring 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 color 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 color, 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 color will be developed in both jars; but if one is filled with spring water, the color in that rapidly becomes dark reddish-black, and one half more water is required to reduce it to the same shade of color 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 color 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 color 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 color, 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 color 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 coloring 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 dugged, the color is imparted by passing the cloth through the dye-beck. On those portions of the cloth on which the mordant is applied, the coloring matter attaches itself in a durable manner, but on

the unmordanted portions the color 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 Colors.*—Such coloring 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 color is afterward effected by exposing the cloth to steam. Some coloring 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 Colors (Padding Style).*—To produce a figure in a mineral coloring material the cloth may be first printed with one of the two saline solutions, and be afterward uniformly impregnated with the other. To obtain a ground of a mineral color, 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 color when afterward 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 coloring matter.

5. *Discharge Style.*—The object of the processes belonging to this style of work is the production of a white or colored figure on a colored 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 coloring matter or the mordant. Chlorine and chromic acid are the common discharging agents for decomposing a vegetable or animal coloring matter, and an acid solution for dissolving a mordant.

6. *For China Blue.*—This is a very peculiar style, and is practised with one coloring 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 coloring 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 color or mordant by pressing it gently on a piece of superfine woollen cloth, called the sieve, which is kept uniformly covered with the thickened coloring matter or mordant by an attendant boy or girl, called the "tearer," (corrupted from the French word *tireur*), who takes the color 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 color. 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 color; hence, if the design contain five or more colors, 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 colors to be applied in figures in straight and parallel stripes, all the stripes may be applied by one block at a

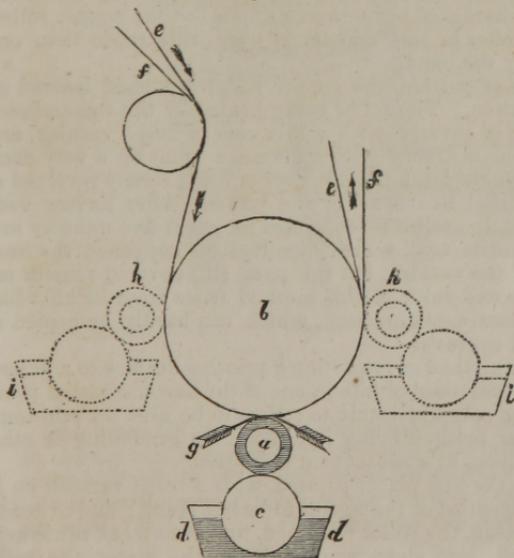
single impression, and the block is also charged with the different colors by a single application to the surface of woollen cloth. The colors to be applied are contained in as many small tin troughs as there are colors, arranged in a line. A little of each color is transferred from the troughs to the woollen cloth by a kind of wire brush consisting of wires fixed in a narrow piece of wood. The color 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 colors 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, the 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 honor 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 colored 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

Fig. 39.



copper. A general idea of the nature of this mode of printing may be conceived with the assistance of the annexed figure; *a* represents 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 coloring matter or mordant properly thickened, and thus acquiring itself a coating of the color, 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 coloring 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 *color 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 color 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 color mixture.

Such is the method of printing calicoes by the roller for a single color; but the mordants or mixtures for two, three, or even eight colors 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 color 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 afterward 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.

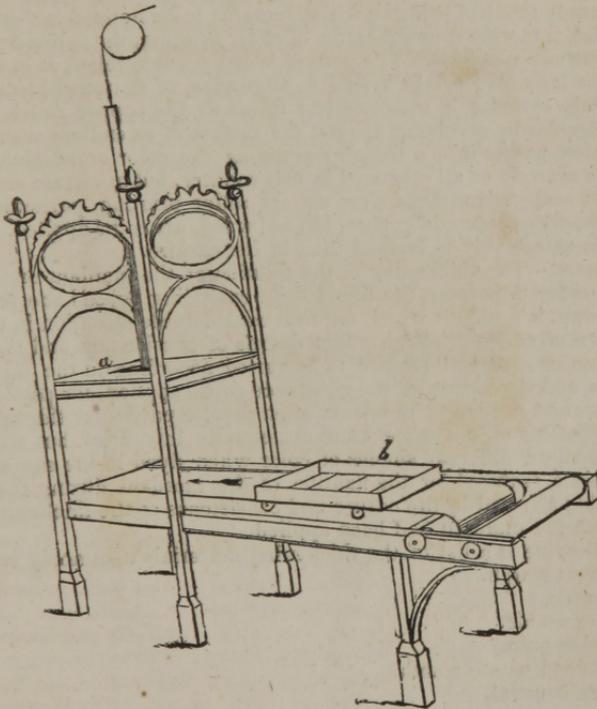
The following ingenious method of imparting a printing surface to a copper roller has been extensively practised of late in one of the best-conducted print-works in Lancashire. It is only applicable to rollers to be used for printing a full ground, sprigs or other designs being left blank, for grounding in other colors 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 afterward, into clean water. From the water, the roller

is transferred to a solution of sulphate of copper and placed in connexion 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 afterward 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 colors may be executed at one impression. A sketch of the principal parts of the press-printing machine is shown 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 colors 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 color, 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 135).

Fig. 40.



The mode of applying the colors 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 arranged in a line five little troughs (or as many as there are colors to be printed), containing the thickened colors. 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 colors to the surface of felt, over which the colors 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 color. This being done, the block is raised, the color-frame withdrawn, and the block caused to descend on the cloth, which it imprints in five rows with different colors. When the block is raised, the cloth is drawn lengthwise 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 color, 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 colors 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, edgewise, of flattened pieces of copper wire. This cylinder is mounted in a frame as the copper roller, and is supplied with color by revolving against the surface of an endless web of woollen cloth, which passes into a trough containing the color 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 coloring 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 coloring 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 color when dyed in the same infusion;\* and the time required for the fixation of the mordant during the ageing is considerably affected by the nature and consistency 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 potato 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.

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

11. Dextrin.
12. Potato 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 coloring 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 115); 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, can not 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 coloring 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 potato 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 colors. 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 coloring matter, when the latter is applied to the whole surface of the cloth.

When the mordant to be printed is colorless, 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 color 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 133.

## I. MÄDDE STYLE.

The madder style is applicable, not only to the dye-stuff from which it derives its name, but to nearly all organic coloring 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. 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 116). Annexed is a specimen of calico in this stage of the process.

No. 1.†



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 124), 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-beck, 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 substi-

\* 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.

† The publishers and the public are indebted for the specimens of *calico-printing processes* to the famed Merrimack Company of Lowell. It may not be generally known that this extensive establishment employs 1,200 females, and sends to the market 250,000 yards of calico per week.

tute 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., shows the appearance

No. 2.



which 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 123.)

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 colors 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 126). 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 coloring 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 130). With madder colors, 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 can not 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 103), 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 afterward subjected have been noticed in the preceding section. The specimen, No. 4, is the finished cloth.

No. 4.



The strength of the mordant, solution of dung substitute, dye-beck, &c., and the details of the process generally, vary considerably for the same coloring matter and mordant, according to the quantity or fulness of the figure, and the depth of its color. 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. Duing, 1<sup>o</sup>, in a mixture of four gallons of dung and three hundred of hot water ; and 2<sup>o</sup>, 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 125), one quart of cleansing liquor (page 124), 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<sup>o</sup> Twad.).

\* The tints of cloths 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.

15. Washing at the dash-wheel ;
16. Drying by the "water extractor" (page 130) ;
17. Folding ;
18. Starching (page 131) ;
19. Passing through the steam drying machine (page 131).

As the quantity of coloring matter which is deposited on the cloth in the dye-beck is much more dependant 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 color may be obtained by the same dye-beck, the cloth having been previously printed with the same kind of mordant at different strengths.

A beautiful pattern is produced by the 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-color 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 119), 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 the mixture of equal parts of flour and starch. The proportion of the thickening ingredient is varied according to the density of the mordant and the fullness 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 may be printed on the cloth with red liquor of spec. grav. 1.105 for dark red spots, and the same liquid of spec. grav. 1.021 for a light red figure. Both solutions must be 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 colors with the same dye-stuff, a variety of colors may be communicated to the calico from the same infusion of coloring matter, provided as many kinds of mordants, or mixtures of mordants, had been previously applied. A pattern 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-color 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 color 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-color machine, after which the cloth is aged for a day or two ; the mordants for the other colors 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-gray color; 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 coloring 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 gray color is obtained in the same way by using very weak iron liquor and a weak decoction of the coloring matter; and a violet color, by applying weak red liquor to the cloth.

Cochineal is another dye-stuff, the coloring 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 afterward produced by other styles. To obtain an amaranth-colored 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 coloring 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 COLORS.

The mere mechanical part of the process is simpler in this than in any other style of calico-printing. The thickened solution of the coloring 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 coloring 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 colors 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 coloring matter is usually determined in such cases by the surface attraction of the tissues frequently assisted by the application of heat. Not many colors applied in this way are remarkable for their permanency. A few topical colors 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 colors 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 8° Tw.,  
 $1\frac{1}{2}$  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 colors to be afterward applied by the madder style. After ageing for two days the black color 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, may be 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:—

$1\frac{1}{2}$  pounds of catechu,  
 $\frac{3}{4}$  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 colors 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 coloring matter by passing the cloth through a solution of bichromate of potash previous to being dyed in the madder-beck.

The chemical change which takes place during the fixation of the astringent principle of the catechu is the absorption of oxygen. Catechu, or its coloring 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, a decoction of logwood, mixed with a tin or an aluminous 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 afterward, a quarter of a pint of oil. 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 or 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 color 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 color 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 colored substance thus produced is a compound of oxide of chromium with the coloring matter of logwood.

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

- 1 gallon of peachwood liquor at 8° Tw.,
- 1½ pounds of starch,
- ½ 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 117), 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.

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

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

1 pound of yellow prussiate of potash,  
 $1\frac{1}{2}$  gills of solution of nitrate of iron of 80° Tw.,  
 3 gills of perchloride of tin of 100°,  
 1 gallon of water, and  
 $1\frac{1}{4}$  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 color is derived from Prussian blue (see page 105).

2. Indigo communicates a faster blue, so far as the action of soap and alkalis is concerned, than Prussian blue; but the latter possesses considerably more brilliancy than the former in its ordinary state. As a topical color, indigo is applied in the form of indigotin, or the hydruret of indigo-blue (see page 100); 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 color 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 color 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 135. The cylinder *c* is dispensed with, the engraved roller itself dipping an inch or two into the color mixture; and the roller is cleaned from the superfluous color by revolving in close contact with one of the sides of the color-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,  
 $2\frac{1}{2}$  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

afterward 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 color. To this solution is afterward 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-colored 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 afterward 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 afterward 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 Colors.*—Very few colors 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, coloring matter, and mordant. Before the printed cloth is exposed to steam, the coloring matter may in general be easily removed by washing with pure water; but afterward 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 colors 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 colors. 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 117); 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 coloring materials and mordants, properly thickened, are applied either by the roller or block. Steam colors are chiefly grounded in by the block to cloths which have been already printed and finished off according to 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 colors; 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 colors is red liquor, mixed with oxalic or some other acid to prevent the precipitation of the compound of coloring 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.,
- 1½ 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 12° 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 afterward 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 cream 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 interduced.

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 color 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 color) 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 color (page 146).

An orange stripe may also be produced by a decoction of Persian berries, the mordant being protoxide of tin only.

A convenient mixture for producing this color 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 color 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.

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 color than that made as No. 1, but the latter is least expensive.

No. 3.

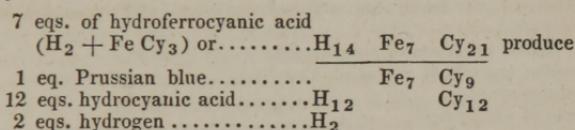
- 1 gallon of water,  
3 to  $3\frac{1}{2}$  ounces of alum,  
 $1\frac{1}{2}$  to 2 ounces of oxalic acid,  
3 to 4 ounces of tartaric acid,  
20 ounces of gum,  
12 ounces of yellow prussiate of potash.

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 color, which changes to deep blue on exposure to the air for a couple of days. The chemical change by which the color is produced during the exposure to air depends on the absorption of oxygen or the removal of

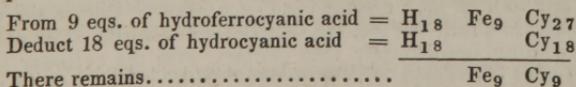
hydrogen; as is evident from the circumstance, that if the goods are passed through a solution of bichromate of potash as soon as withdrawn from the steaming cylinder or chamber, the blueish-white changes to deep blue immediately. If the red prussiate of potash is employed instead of the yellow prussiate, the cloths acquire the proper blue color during the steaming, and the depth of the color is not sensibly increased by exposure to air or to a solution of bichromate of potash.

The blue coloring 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,



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 color 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 odor 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. The 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,



On exposure to the air, this compound of iron and cyanogen, the probable constitution of which is represented by the formula Fe<sub>6</sub> + 3(Fe Cy<sub>3</sub>) absorbs

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

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  $\text{Fe}_2\text{O}_3 + (\text{Fe}_4 + 3(\text{Fe Cy}_3))$ .

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 color has not been long in general use for application to calicoes. The color 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 quantity 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 color is about thirty minutes.

After the color 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 colors 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 coloring 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 colors 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 colors only a pattern containing a design in lilac, pink, red, yellow, black, and dark orange red, the cloth may be printed by the five-color machine.

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 (page 149), one containing weaker cochineal or peachwood liquor than the other;

By the fourth roller, with the mixture for the yellow (page 149);

By the fifth roller, with the mixture for steam black (page 148);

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 colors, which is susceptible of a great variety of interesting modifications.

1. The cloth is printed by the three-color 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 (see page 146), 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 152), and steam yellow (page 149), 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-color 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 146). 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 150), and steam yellow (page 149), 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.

As an example of the combination of madder colors with steam colors, for the red and chocolate stripes, the cloth may be 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 may be applied by the block.

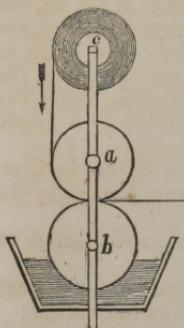
### III. MINERAL COLORING MATTERS.

Mineral coloring matters are adapted, not only to the production of designs on a white or colored ground, but also to form a ground for the reception of a design in other colors. To impart the color 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 color, or else the cloth may be

padding in one of the solution and be afterward winced in the other. To produce a design in a mineral coloring matter on a white or colored 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 131), the thickened liquid being contained in the trough *a*.

Fig. 41.



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 thickened. The calico is first rolled around the cylinder *c*, and then passed in the direction of the arrow between 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 131, or through the hot-flue. If the color 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.

**Prussian Blue.**—More than one method of applying this coloring 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.**—A beautiful yellow and orange 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 containing a little size, then dried, passed first through a weak solution of carbonate of soda, and afterward 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 afterward 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 afterward 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 blue and black may be merely spirit colors.

Different shades of green are given to cotton goods by a mixture of chrome-yellow with Prussian blue. The coloring materials may be applied consecutively, or at once from mixed solutions; the cloth being first padded, in the latter case, with a mixture of acetate of iron and nitrate of lead, and afterward 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 color 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 147, 148. 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 afterward 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 permanganate and a mixture of the acetate with the protosulphate, obtained by adding from one part to three parts of acetate of lead (pyrolygnite) 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."

A buff color is produced by iron buff.

To impart a buff ground, the pieces are padded in buff-liquor of any strength between 2° and 10° Tw., according to the shade of color 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 afterward 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 become 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.

\* 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.

*Manganese Bronze.*—A brown ground is produced by manganese bronze or peroxide of manganese.

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 by-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 colorless. Having been allowed to settle, the solution is decanted and concentrated by evaporation.

To impart a dark bronze ground such as that above described, 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 color, 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 colors, namely, antimony orange, arseniate of chromium, orpiment, and prussiate of copper (see page 104, *et seq.*)

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

1. Print the cloth by the four-color machine with the mordants for black, purple, and two reds (see page 143);
2. Age, dung, dye in the madder-beck, clear and dry;
3. Print by the two-color 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 rinse in water;
5. Dry and print by blocks with the mixtures for steam blue (page 150), and steam yellow (page 149);
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.

#### IV. RESIST STYLE.

The object of the resist style of work is to produce a white or colored design on a colored 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 development of color, when the whole surface of the cloth is afterward 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 coloring 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; as in the combinations of such a style of work with madder colors and steam colors. 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 afterward pegged in by blocks, and the steaming is performed in the usual manner. The mixture for the green in the above specimen is quite similar to that described at page 152; that for the yellow was made by mixing a quart of red liquor of spec. grav.  $8\frac{1}{2}^{\circ}$  Tw., with a gallon of berry liquor of  $2^{\circ}$  Tw.

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

2. *Resist 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 afterward applied, it is seldom used of a higher density than  $2^{\circ}$  Twad.

Designs in black, lilac, and white, on a lilac ground, can be produced by adapting the resist style of work to madder colors. The printing for such a pattern may be performed by the three-color machine in the following order:—

By the first roller; the resist, which may be either lemon-juice of spec. grav.  $2^{\circ}$  or  $3^{\circ}$  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.  $8^{\circ}$  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.  $1\frac{1}{2}^{\circ}$  Twad., thickened with four pounds of British gum to the gallon.

\* 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.

The application of the mordant for the ground may be made by the padding machine, (fig. 41, page 154), 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 a 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-color 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 colored ground; it is commonly mixed with red liquor, as the deposition of the insoluble subsulphate 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 afterward 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 a lilac ground, 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 colors, 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 colors 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 colors; for which purpose the free acid is quite inapplicable, as it would dissolve the mordant on the cloth in combination with the coloring-matter. If the dyeing of the cloth with mad-

der is performed at two operations, neutralized lime-juice is generally preferred to the fat resist for protecting the red, lilac, and white figures; but if the madding is to be completed at one operation, the fat resist must be used.

3. *Resists for the coloring matter.*—The production of a white or colored pattern on a colored ground by the direct action of a resist on a coloring matter, is chiefly practised with indigo, at least in the printing of calicoes. 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 binarsenate 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 colorless hydruret of indigo, or indigotin (see page 244). 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 afterward 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 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 in the blue-vat, as if, for instance, a design had been previously applied in madder-colors, 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 colors has to be protected.

A white pattern can be produced by such a process as that just 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

\* Commonly called the peroxide.

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 color is obtained.

The composition of the resist paste is varied according to the depth of color 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 colors 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 hogs'-lard,
- 2 quarts of gum-senegal water, containing 6 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 colored 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 color, or else the mordant for a coloring 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 afterward 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 carbonate 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 afterward 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 160), 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 colored figure on the indigo ground, is by combining with the resist paste a mordant for a vegetable coloring 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 afterward 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 159, but with only eight hundred gallons of water;
2. Rinsing in water;
3. Dunging or branning;
4. Washing at the dash-wheel;
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 afterward 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 160.
- 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-color machine, and be treated afterward 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 (page 145). 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° Tw. 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 color capable of being applied by the madder style, the cloth may be treated as follows:—

1. Print with the white resist, No. 1, page 160.
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 afterward 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 afterward printed on the protected parts, by the two-color 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 160. It is then dipped into the blue-vat and dyed in the usual manner.

To procure a pattern containing a design in orange, crimson, and white on a blue ground, the cloth is printed by the two-color machine with the mixture of salts of copper and salts of lead (page 160), on the parts to be orange, and with a white resist on the parts to be crimson and white. After being dipped

\* 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.

into the blue-vat and cleared in dilute sulphuric acid, it is winced in the following liquids: 1<sup>o</sup>, solution of carbonate of soda; 2<sup>o</sup>, solution of bichromate of potash; and 3<sup>o</sup>, 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 afterward printed by block on parts of the white with the mixture for a topical or steam red or crimson.

A design in blue, yellow, green, red, and white on a dark chocolate ground, was produced by combining the lazulite style with a topical color. 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 160, on all the parts required to be yellow and white; with the mixture of red liquor, sulphate of zinc, and acetate of copper, made as described at page 161, 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 color 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 coloring design previously applied in madder colors. To produce this pattern, the cloth is treated as follows:—

1. Print by the two-color 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 spaces having catechu only.

#### V. DISCHARGE STYLE.

The manner of producing a white or colored pattern on a colored ground by the topical application of a "discharger" to a cloth already mordanted or dyed is applicable to both mineral and vegetable coloring matters. Like the resist paste in the preceding style, the discharger may act either on the coloring 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 coloring materials are obtained from different

\* 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, afterward applied as a blotch. Such a mixture is designated (not very appropriately), *neutral paste*.

classes of chemical substances according to the nature of the coloring matter to be removed. The essential property required in a discharger is that of converting the substances on the cloth into colorless or soluble products, which may be removed from the cloth so as not to interfere with the subsequent application of a coloring material to the parts discharged.

1. *Dischargers for Coloring Matters.*—The materials used as dischargers for vegetable coloring principles are chlorine and chromic acid, the bleaching powers of which have before been alluded to (page 98).

To effect the topical discharge of a vegetable coloring 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 color 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 colors immediately; so that a cloth dyed with such colors may remain for some minutes in contact with a solution of chloride of lime without any deterioration in color. 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 coloring matter on those parts of the cloth. Almost the only colors to which chlorine can be thus applied as a discharger, are Turkey-red and other madder colors and indigo, as the more delicate colors are easily discharged by chloride of lime alone.

A white discharger adapted for all madder colors 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 downward 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 color.

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 the ground is considerably increased.\*

After the production of a white figure on a colored ground by the application of the acid discharger and immersion in the solution of chloride of lime, colored figures may be applied either to the ground or to the white figure by grounding in topical colors by the hand-block. A common method of imparting a colored figure is by mixing with the acid discharger one of the two solutions necessary for producing a mineral coloring material. For example, to impart a yellow figure to a piece of cotton dyed with Turkey-red, the cloth is treated in the following manner:—

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 a 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 coloring matter is chromic acid, which produces the decomposition of the coloring matter, by virtue of its oxidizing power, the chromic acid becoming reduced to the state of green oxide of chromium. The vegetable coloring 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 color of the indigo on the cloth is destroyed immediately on the appli-

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

cation 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 coloring 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 coloring 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 coloring 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 afterward 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 afterward 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 (page 156), 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 coloring principle of a vegetable dye-stuff, as peachwood, 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 colored designs may be applied to the manganese ground by afterward dyeing such goods in various dye-becks.

To impart a design in white, blue, and yellow, on a bronze ground, 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 color 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 afterward 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 colored designs may also be applied by combining with the discharger, the materials for the production of a topical color. 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 peachwood 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 is obtained by applying to the colored 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 colored 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-colored 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 160);

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 colored figures on a colored ground, referable to the discharge style of work, is by the removal of the mordant previous to the application of the coloring 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 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;\*

4. The cloth is afterward 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 coloring 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 157); 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, by the discharge 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;

\* 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. 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 160, 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, 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 (page 158). 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 colored figures on colored 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 coloring 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 afterward printed with the acid solution of the protochloride. Wherever the salt of tin is applied, the color of the cloth changes from black to red, through the transference of the coloring 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.

#### VI. 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 color, associated with white.

\* 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 163. The cloth is first printed with the white cupreous resist (mixed with a free acid, when a very well defined figure is required), and afterward with the chocolate resist (page 163), 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, referred to at page 150.

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, and gum or starch, and water; the proportions of gum or starch and water being varied according to the depth of color 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 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 takes place in these successive operations are rather complicated, but admit 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.  $5^{\circ}$  Twad. (1.025). It is afterward 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,

15 $\frac{3}{4}$  pounds of indigo, in coarse powder,  
 3 $\frac{3}{4}$  pounds of orpiment,  
 22 pounds of copperas, and  
 9 $\frac{1}{2}$  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 afterward added; but if a very thick

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

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

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; and 2°, No. 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:—

	Quantity by measure of above mixture.	Quantity by measure of water or gum-water.	Quantity of indigo in 1 gallon of the mixture.	
			lbs.	oz.
1.....	1.....	0.....	2.....	0
2.....	1.....	$\frac{1}{2}$ .....	1.....	$5\frac{1}{2}$
3.....	1.....	$\frac{3}{4}$ .....	1.....	$3\frac{1}{4}$
4.....	1.....	1.....	0.....	0
5.....	1.....	2.....	0.....	$10\frac{3}{4}$
6.....	1.....	3.....	0.....	8
7.....	1.....	5.....	0.....	$5\frac{1}{4}$
8.....	1.....	7.....	0.....	4
9.....	1.....	9.....	0.....	$3\frac{1}{5}$
10.....	1.....	12.....	0.....	$2\frac{1}{2}$
11.....	1.....	16.....	0.....	$1\frac{1}{4}$

The darkest of the two shades of blue in this style of printing is 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 are thickened with two pounds of British gum per gallon, and are applied at once by the two-color 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  $3\frac{1}{2}$  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 color 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° Twadell (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 color; 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.

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*Printing of Mousselin de Laines, Silks, Chalis, &c.*—The fixation of coloring matters on fabrics of silk and wool is commonly effected by the process of steaming. No mineral coloring material, with the exception of Prussian blue,

is applied to these tissues; nor is it usual to impart to them coloring 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 137) have been substituted.

The color mixtures for *de laines*, which are formed of cotton and wool, should be of such a nature as to afford a uniform deposit of coloring 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 color to the *laines*, is a mixture of the steam blue for cotton (page 150) 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 afterward perfectly bleached by exposing the dyed *de laines* to a dilute solution of bleaching powder. The cotton thread is sometimes dyed of another color, 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 (page 107). 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 colors for woollen goods and those for cotton goods (page 148), is that the former contain more free acid than the latter, or that the coloring 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 colors 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 150), 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<sup>o</sup>, boiling in a solution of soap and carbonate of soda to remove the "gum;" 2<sup>o</sup>, passing through dilute sulphuric acid; and 3<sup>o</sup>, 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 afterward 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 colored designs is by means of steam colors, 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 color-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 color may be communicated to the silk or wool by exposing the stuff to the action of nitric acid. The color 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 the 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 sandstone 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. Colored 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 color of the ground may be afterward modified or completely altered by dipping the cloth in some dyeing liquid, the figures being still pro-

tected, 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 afterward exposed to the action of steam, and is lastly boiled in soap-water to brighten the orange.

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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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MANUFACTURES, ARTS, AND DOMESTIC ECONOMY.

EDITED BY

**E. A. PARNELL,**

AUTHOR OF "ELEMENTS OF CHEMICAL ANALYSIS;" LATE ASSISTANT CHEMICAL LECTURER IN THE  
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WITH NUMEROUS WOOD ENGRAVINGS, AND OTHER ILLUSTRATIONS.

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