"over-scoured," since the colour goes back a little, *i.e.* loses some of the blue tinge, in drying.

Black and Blue Dyeings with Logwood on Wool.

Logwood is used in the form of chips or as an extract, and occasionally is subjected to a process of oxidation termed "fermentation," the object of which is to convert the hæmatoxylin present in the wood into the true pigment hæmatein.

According to Von Cochenhausen, the different constitution of the chips and extract (which merely contain hæmatoxylin) from that of the fermented product should lead to a modification in their method of employment, which, however, is disregarded in practice. This observer's view is that, in the case of the unfermented wood or extract, the hæmatein is only produced during the operation, either as a result of prolonged boiling or of the oxidising action of the mordant on the hæmatoxylin; consequently these materials should preferably be used, in conjunction with iron and copper mordants, for dyeing wool that has been mordanted with potassium bichromate and sulphuric acid. If, however, the available mordants have no oxidising action, *e.g.* alumina mordants, or potassium bichromate in presence of an organic acid, then better results will be obtained with fermented logwood. Finally, he considers that the fermented product should never be used after the said oxidising mordants, since in such event the destruction of the hæmatein, which is readily oxidised to brown substances, is to be feared.

The fermentation is performed in a primitive manner, usually in the dyeworks, by spreading the logwood chips in irregular heaps, which are then moistened with water, or weak solutions of alkali, and turned over at intervals.

A more rational method of procedure is as follows:—The chips are laid in heaps, about eighty inches in depth, on a well-ventilated upper floor, where they are slightly moistened and left for several days or weeks, according to the time of year. The completion of the process may be recognised from the appearance of the wood, which, when properly fermented, is of a dark red-brown colour and exhibits in places (if sufficiently rich in pigment) a greenish incrustation of hæmatein crystals, with metallic lustre. The wood is then spread out in thinner layers and dried at about 50° C. in order to prevent further oxidation, which might prove injurious to the hæmatein.

Logwood extract is prepared in various ways, which may be divided into two chief classes,—with and without pressure; the

former furnishing a larger yield, whilst the latter gives the better quality product. The yield stands in direct relation to the degree of pressure and temperature employed for the extraction.

In extracting under ordinary pressure, which method is adopted in some works, the comminuted and unfermented wood is placed in a diffusion apparatus of the type used in sugar-refining, and is extracted with warm soft water, the sole pressure applied being that of a column of water about 10 feet high. If the product be intended for the calico-printer, the extraction is carried on at 60° C., but if for dyeing, the temperature is increased to 80°. The operation will be finished in about five to six hours, and the residue is used as fuel. Extraction at 80° C. should give a yield of at least 25 per cent.; at lower temperatures it is naturally smaller, but of better quality. If the American method be employed—extracting in closed vessels—the pressure should never be less than two atmospheres, and the quality suffers in proportion as the yield exceeds 30 per cent.

The solution obtained by one or other of the above methods is clarified by settling, and then concentrated to 30° B. *in vacuo*. The extract for printer's use, which must be entirely free from solid matters, is filtered before concentration, and the latter process is frequently stopped when the density measures 20° B. Solid extract is also made, but is less suitable for use—especially in printing—since in the preparation no trouble is taken to remove impurities, without which latter, indeed, the production of a solid extract by evaporation is impossible. In point of dyeing power, 6 parts of solid extract correspond to about 10 parts of a 30° B. liquid extract.

As regards the quality of the wood to be used, little can be said on this point generally, cheap logwoods being occasionally better adapted for the production of extract than dearer sorts. Extensive use has latterly been made of roots, chiefly from Jamaica, in the production of extract. The very fine extract sold under the name "hæmatein" is prepared from Laguna logwood.

The literature on the preparation of logwood extracts is comparatively large, but contains so many unreliable and contradictory reports that it will be left out of consideration here. There are also a large number of patents dealing with improved methods of manufacture and purification. Thus, to give an instance, Foelsing's patent proposes to extract fermented logwood and pass an electric current through the resulting solution kept under pressure, the object of this treatment being to de-resinify the extract. With regard to the technical value of this and similar processes no information is available.

Logwood is also extracted by two methods—with and without pressure—in dyeworks. In the latter case the chips are put into bags and boiled in water for two hours in a wooden vat. In the pressure method the chips are put into a small upright boiler and boiled twice—a quarter of an hour each time—with water, under a pressure of at least two atmospheres. A frequent source of error in this method is to work with too large a quantity of chips at a time; properly the boiler should be only about two-thirds full.

The black dyeing of wool with logwood is an art of great antiquity, there having been a guild of black dyers as long ago as the eleventh century. Formerly a fast black was produced on a vat bottoming, but at present, from motives of economy, this method has almost entirely disappeared, leaving the field to the three following processes:—

1. Iron black, or Salzburg black (so called because frequently produced with the aid of "Salzburg vitriol," consisting of ferrous and copper sulphates), with ferrous sulphate and copper sulphate as mordants.

2. Chrome black, with potassium bichromate and copper sulphate as mordants.

3. Single-bath black, mordanted with ferrous sulphate, either alone or in conjunction with copper sulphate.

An important point is the quality of the water used for dyeing, softness being essential; so that hard water must be corrected with acetic acid. The resulting calcium acetate has a favourable influence on logwood dyeings, for reasons that have already been discussed in the chapter on Mordants.

Iron black is the oldest wool black known; the method is employed in a number of modifications, but only the simplest and most rational form will be described. The material is first mordanted with 10–15 per cent. of ferrous sulphate, 4–6 per cent. of copper sulphate, and $1\frac{1}{2}$–2 per cent.—sometimes as much as 5 per cent.—of potassium bitartrate. Loose wool requires more mordant than piece goods. In the case of finer goods the proportion of bitartrate is increased, the result being that the material is dyed through better. Dyeing then follows. Nowadays extracts are chiefly used for dyeing loose wool, yarns, and the finer piece goods, logwood chips serving for lower-class goods. The black obtained by the use of extract is dearer but finer, and has a cleaner appearance than that from chips. A very handsome blue-black can be obtained with 10 per cent. of solid extract, the quantity of chips required for dyeing varying between 30 and 60 per cent., according to their richness in dye and the quality of the goods to be treated—the finer the material the larger the amount of dyewood. Some

dyers prefer the inferior kinds of logwood (*e.g.* Monte Christo) to the better sorts for this purpose. To convert the bluish tinge characteristic of logwood blacks into deep black, the dye-bath must receive an addition of about 2 per cent. of 30° B. fustic extract. The goods are entered hot, raised to 100°, and boiled for an hour and a half to two hours. The after-treatment with copper sulphate is frequently given in order to deepen the black and remedy defective mordanting. When mordanting has been correctly performed the dye-bath will be of a wine-yellow colour. After dyeing, the goods must be thoroughly washed—piece goods receiving an addition of fuller's earth—to dissolve the adherent unfixed particles of dye. If this be omitted the colour will rub off to a considerable extent.

Chrome Black.—The production of a deep logwood black with a chrome mordant alone is impossible, this method furnishing a blue-black which, moreover, is fugitive under the influence of light. Consequently in practice the so-called chrome black is produced with the aid of copper sulphate, the resulting colour being deeper and faster to light; the shade depends on the amount of copper sulphate employed.

The wool is mordanted with 3 per cent. of potassium bichromate, 1½–3 per cent. of copper sulphate, and 1½ per cent. of sulphuric acid; and is then dyed in the same way as for iron black. To ensure the black rubbing off as little as possible, which is an important consideration in yarns intended for working up along with white, the wool is returned to the mordanting bath for a short time after leaving the dye-bath.

Single-bath black is produced in two ways. Formerly a common black was obtained by dyeing the goods for some time in a decoction of logwood and 5–6 per cent. of sumach, and then darkening with ferrous sulphate.

This, however, rubs off more extensively than any other black dyeing on wool, and its use is therefore restricted to common wools and yarn waste. If a single-bath method appears advisable, either on the score of cheapness or because the prolonged boiling in the two-bath process is likely to injure the quality of the goods, then the dye-bath is prepared with 4 per cent. of ferrous sulphate, 2 per cent. of copper sulphate, 2 per cent. of oxalic acid, 10 per cent. of 30° B. logwood extract, and ½–1 per cent. of fast yellow. After boiling the bath liquor and cooling it down with cold water, the goods are entered and boiled for an hour.

An essential condition to success in this method is the use of a proper quantity of oxalic acid, which reagent is added to dissolve a portion of the colour lake formed in the bath, since, like other

textile fibres, the wool can only absorb dyes that are presented in the dissolved state.

If the dye-bath contain too little oxalic acid it will seem quite turbid, owing to the greater part of the colour lake remaining undissolved; consequently it will not furnish a full black. On the other hand, if the oxalic acid be in excess, not only will the whole of the colour lake be dissolved, but its absorption will be retarded. In such case the bath is quite pale, and naturally will not give a full black.

The single-bath method is also applicable to other dyeings; thus, a good navy blue can be produced in this manner with logwood, acid violet, and acid green, whilst logwood and cloth red give a fast brown. For this last purpose the single-bath method was first applied, by Oehler, to replace santal.

A logwood dyeing still frequently practised is the so-called logwood blue, which is a handsome colour, but very fugitive to light. It is produced by mordanting the goods with 8 per cent. of alum, $\frac{1}{2}$ per cent. of copper sulphate, 1 per cent. of bichromate, 4 per cent. of bitartrate, and 2 per cent. of oxalic acid, and then dyeing with logwood; the blue obtained by the use of alum alone would be too dull.

The washing fastness of the logwood dyeings is good; their fastness to light depends on the mordant used, copper and iron mordants giving fast colours, the other mordants fugitive shades. Iron black is very fast to light, but chrome black and logwood blue are fugitive, though the chrome black becomes satisfactorily fast when produced by the aid of copper mordant. On the other hand, iron black is very sensitive to acid; whilst chrome black is quite fast in this respect, dusts off to a smaller extent, and leaves the wool softer, on which account it is preferred to iron black for yarn-dyeing.

Application of the Mordant Dyes to Silk.

The mordant dyes are but rarely applied to silk; in fact, only when fastness to soap is desired. As in wool-dyeing, the chrome mordants are the chief ones used, alumina mordants being only resorted to for red and orange, and iron mordants for black.

Of the mordant dyes that are suitable for silk, mention may be made of the following:—Alizarine yellow GGW, anthracene yellow, mordant yellow, diamond yellow, carbazol yellow, galloflavine, cloth brown, diamond brown, alizarine orange, alizarine red (the wool marks), Kalle's cloth scarlet, galleine, anthracene blue, cœruleine, diamond green, alizarine black, diamond black, etc. As a matter

of fact, however, only a few are in general use, viz. alizarine red (*e.g.* the SX mark), alizarine orange, galleine, and cœruleine.

The *modus operandi* is as follows:—A very rich bast-soap bath is prepared of equal parts of (weak) bast-soap solution and water, which is then neutralised with acetic acid, for pale and medium shades, or made slightly acid for dark shades. The mordanted silk is then entered cold, worked about in the cold bath for twenty minutes or so, then raised to 90–95° C. in about an hour, and kept at that temperature for an equal time. When soft water is used an addition of calcium acetate must be made to the bath for alizarine red.

After dyeing, the goods are rinsed, energetically soaped by boiling for a quarter of an hour with about 2 parts of soap per 1000, then rinsed again, and finally brightened with acetic or oxalic acid (20–25 parts of 6° B. acetic acid per 1000, lukewarm) for ten minutes.

Logwood black plays a particularly important part in silk-dyeing, and, indeed, forms a special branch of this industry, quite distinct from colour dyeing.

The black dyeing of silk is one of the most difficult tasks the dyer has to perform. The art of the dyer consists in dyeing the silk and loading it to different degrees, in all imaginable shades of black, without impairing its lustre. The extent of the loading to be obtained is highly divergent, the minimum being to parity ("*al pari*"), *i.e.* the weight lost in scouring has to be made up again in loading; whilst the maximum loading attains 400 per cent. This latter degree was formerly reached in the case of souple silk for umbrellas, but is now almost entirely discontinued. The usual loading is about 50–60 per cent., light, souple umbrella silks being increased to the extent of 20–30 per cent., and heavy souples for the same purpose by as much as 190–200 per cent.

The requirements exacted of black silk in respect of shade, feel, and lustre are extremely varied, and the method of dyeing has to be modified in almost every case; consequently only the main outlines of the process can be sketched here.

The silk for black dyeing is treated almost exclusively in the state of hanks. The dye used is generally a home-made preparation, a 0·1° B. decoction of logwood chips, the commercial extracts, which are prepared from more highly concentrated decoctions, containing yellow dye-stuffs, in addition to haematoxylin, and being therefore unsuitable for the black dyeing of silk: in fact, the handsome blue-black known in France as "*noir bleu bleu*" cannot be obtained by the use of commercial extracts.

The silk is dyed in either the souple or fully scoured state. In the latter event, the *modus operandi* is as follows:—The silk is first

mordanted with Rouil mordant, as described in the chapter on mordants; after which it is blued by treatment in a bath containing potassium ferrocyanide and hydrochloric acid, whereby Berlin blue is developed on the fibre. In the next place the silk is entered into a hot bath of catechu, to which is gradually added a certain quantity of tin salt, the proportion of this latter varying directly with the degree of loading required. Then follows a second bath of catechu, this time without tin, and this is succeeded by the actual dyeing with the aforesaid decoction of logwood in presence of soap. The final operation is that of brightening, which consists of treating the silk in a bath containing emulsified olive oil and acetic acid or citric acid.

This is a broad sketch of the process, which is performed in various modifications.

Occasionally, to shade the dyeing, the silk is topped with fuchsine or methylene blue in a fresh bath. To obtain a blue tinge, iron pyrolignite must be used, the following treatment being interposed between the logwood bath and the brightening process:—

A bath of iron pyrolignite;

A cold, weak logwood bath;

A cold, weak catechu bath;

A bath of soap and logwood.

To obtain a still blue-black, the treatment with iron pyrolignite must be repeated after the second logwood bath.

According to the type of black required, various modifications are introduced into the several stages of the process; thus, for example, a single mordanting and a single weak catechu bath without tin are sufficient for light souples; whereas, for a rich black ("*noir riche*") the silk must be entered five times in a strong mordant bath and two catechu baths, one of them containing tin.

For light cheap black, the blueing with potassium ferrocyanide is omitted, its place being taken by a bath of alkali blue, which, however, must be used before, and not after, the mordanting with iron. For the sake of cheapness, catechu may be replaced by chestnut extract and divi-divi for heavy souples. Finally, also the brightening process is in many instances omitted, especially when the souple is intended for moiré, in which event a softening treatment is pursued.

Some souples that are not required to be deep black are dyed, without logwood, by merely treating them with alternate baths of an iron mordant and a tannin mordant.

The particulars of dyeing two different styles of black on silk are given below.

1. *Noir Riche, with* 50–60 *per cent. of Loading.*

1. The scoured silk is mordanted five times in a 30° B. bath of Rouil mordant.

2. Entered cold in a bath of 20 per cent. potassium ferrocyanide and 25 per cent. of hydrochloric acid, the latter added in two portions.

3. The silk is entered in a bath containing 200 per cent. of catechu, at 80° C., and, when the bath has cooled down to 65° C., an addition of 15 per cent. of tin salt is given, the silk being left in the bath for five hours longer.

4. The silk is entered in a boiling-hot bath containing 100 per cent. of catechu, and is left therein overnight.

5. Dyeing with a 0·1° B. decoction of logwood and 50 per cent. of soap.

6. Dyeing with fuchsine in a bast-soap bath qualified with acetic acid, at a temperature of 40° C.

7. To the foregoing bath is added, for brightening the silk, a mixture of 5 per cent. acetic acid and 4 per cent. of olive oil in the form of an emulsion.

2. *Trame Noir Souple Persan, with* 150–160 *per cent. of Loading.*

1. Treat with 5 per cent. of hydrochloric acid at 50°. Squeeze.

2. Mordant twice in an 18° B. bath of Rouil mordant.

3. Treat in a cold bath containing 30 per cent. potassium ferrocyanide and 40 per cent. of hydrochloric acid. Wash.

4. Enter in a decoction of logwood (density, 0·03° B.), at 40° C.

5. Enter in a bath of 500 per cent. of catechu, at 60° C.; heat and add 10 per cent. of tin salt when the temperature reaches 70° C., and an equal amount at 80° C. The entire operation takes a day; the goods are then washed with water at 40° C. and drained.

6. Treat for an hour in a bath of 100 per cent. of soap, at 60° C.; drain and dry.

7. Enter in the above catechu bath for one hour; wash.

8. Enter, at 50° C., in a bath containing 75 per cent. of soap and a little methylene blue.

9. Enter, at 40° C., in a bath containing 3 per cent. of gelatin and 20 per cent. of acetic acid.

10. Brighten with 4 per cent. of oil and 15 per cent. of acetic acid, at 40° C.

Application of the Mordant Dyes to Cotton.

The most important mordant dyeings on cotton are the Turkey-red process, several catechu dyeings, and, in a secondary degree, logwood black. In this branch, and especially in the dyeing of loose cotton, there still exist various irrational methods which have been handed down by tradition, and, having been based on the dyeing of wool, are really unsuitable for cotton. These dyeings are effected by the aid of dye-wood extracts, the cotton being boiled in dissolved mordants—alum, bichromate, copper sulphate, etc.,—then left exposed to the air all night, and dyed next day in a hot bath. Single-bath dyeings, darkened by after-chroming, are also still not infrequently performed. Leaving these out of consideration for the present, there are really two methods in use for dyeing cotton with mordant dyes. The chief of these consists in mordanting the goods and then dyeing in a bath, which, with few exceptions, should be neutral. The goods should first be treated in the cold dye-bath for about a quarter of an hour, the temperature being then raised, in about three-quarters of an hour, to 60–70° C., and there maintained for three-quarters of an hour, after which the goods are washed, and, in some cases, soaped hot or warm.

By this means a series of Bordeaux, garnets, browns, and violets are obtained with alumina alone or alumina and iron as mordants, on piece goods, the dyes used comprising alizarine, quercitron, redwood, rubine (impure fuchsine), and methyl violet, and being combined in pairs or threes—not employed all together. Thus brown shades are produced with alizarine, quercitron, and logwood, after mordanting with alumina and iron mordants, the colour being shaded, if necessary, with rubine or methyl violet. Strangely enough, the low fastness of the two latter dyes is not manifested in these combinations.

Of late a variety of dyeings for the production of discharge effects on piece goods have been performed by the aid of chrome mordants, the dye mostly concerned being anthracene brown.

A second method for dyeing (mainly piece) cottons with mordant dyes is that of Erban and Specht, which, though originally designed for Turkey-red, is also applicable to the production of a whole series of lighter colours. It consists in first padding the goods with an ammoniacal solution of dye, then drying, entering in a mordanting solution, redrying, and afterwards effecting the combination of the dye and the mordant by steaming.

Turkey-Red Dyeing.

By the name "Turkey-red" is understood a red dyeing effected on cotton by the aid of alizarine, alumina, lime, and fatty-acid compounds. For several hundred years this colour, thanks to its beauty and fastness, has played a part comparable to that of indigo in blue dyeing. It probably originated in India, and was brought from Turkey to France, where the method of performance was published by the Government in 1765, and whence the process spread to other European countries.

The production of Turkey-red was at one time the monopoly of a few manufacturers, who kept their operations a profound secret. In more recent days, however, this industry, which previously remained without any important changes, has made rapid strides through the supercession of madder by artificial alizarine, and the introduction of modern apparatus. The principal modification of of all resulted from the introduction of Turkey-red oil, which has entirely replaced the older process for dyeing piece goods, and to a great extent in dyeing yarns as well. The superiority of the new method over the old chiefly resides in its greater brevity, the production of the red now taking only as many days as formerly weeks.

A good deal has been written with regard to the formation and composition of the colour lake here in question, and considerable research work has also been carried on in this connection. It was first discovered by Rosenstiehl that the formation of the lake from alizarine and alumina could not take place except in presence of lime. This was confirmed by Liechti and Suida, etc., it being also found that all Turkey-red dyeings contain lime.

The principal results of the labours of Liechti and Suida may be briefly recapitulated. If a solution of aluminium sulphate be treated with a corresponding quantity of an ammoniacal solution of alizarine, there is formed a dark red precipitate, consisting of a combination of one molecule of alumina with three molecules of alizarine.

This "normal aluminium alizarate" is readily soluble in water; whilst the basic alizarates, which contain a smaller proportion of alizarine, *e.g.* 1–2–3 molecules to two molecules of alumina, are insoluble in water and alcohol. Alkaline solutions of the normal or basic alizarates can be mixed with Turkey-red oil or soap solution without undergoing decomposition; but, on the alkali being neutralised, red precipitates are thrown down.

Liechti and Suida also prepared the calcium compounds of alizarine. Normal calcium alizarate, $CaO \cdot C_{14}H_6O_3$, is formed, as a

blackish violet precipitate, by the action of lime water on alizarine. The acid and basic alizarates, which are similar in appearance, pass over into the condition of the normal salt when warmed, from which it must be concluded that the normal alizarate is also formed during dyeing. Mixed with Turkey-red oil, and steamed after printing on cotton, this salt is decomposed into alizarine, calcium sulphate, and the corresponding fatty acid compound of lime. Therefore, since the steaming of the dye in presence of Turkey-red oil also occurs in the process of Turkey-red dyeing, it cannot be assumed that calcium alizarate is present as such in Turkey red. On the other hand, one is obliged to consider lime as an essential constituent of the colour lake, the latter being therefore assumed to be an aluminium-calcium-alizarate. According to Liechti and Suida, a "normal red" has the composition $Al_2O_3 . CaO . (C_{14}H_6O_3)_3$. To produce this red upon the fibre the goods should be charged with 0·198 grm. of alumina (Al_2O_3), and be dyed with 7 grms. of alizarine (in the form of 20 per cent. paste) per metre of cloth. In comparison with the above formula all the reds met with in practice exhibit an excess—generally considerable—of alumina, which, however, neither improves the beauty nor the fastness of the colour.

The amount of lime taken up in the dyeing is determined by the quantity of alizarine present; conversely, a material containing more lime will absorb a larger proportion of alizarine. When free calcium alizarate is present the red will have a brownish look; its beauty and brightness will be greatly improved by steaming in presence of Turkey-red oil, as will be evident from what has been stated above.

So far the results obtained by Liechti and Suida; nevertheless, the part played by the fatty acids in Turkey-red dyeing has not yet been clearly defined. We know, from experience with the mordants, that fatty acids exert a fixative influence on alumina as on other mordants, apparently by the formation of the corresponding fatty acid salts. However, whether the compound of alumina with the fatty acid combines with the alizarine in the formation of Turkey-red, or whether the alizarine precipitates the fatty acid in order to itself combine with the alumina alone, is a question that cannot yet be decided.

Since the Turkey-red lake always contains an excess of alumina and fatty acids, it may be justifiably assumed that a portion of the fatty acids is contained, as an alumina soap, in the dye. This assumption also affords a plausible explanation of the difficulty experienced in damping yarns dyed with Turkey-red oil, and the hardness of such yarns. To some extent also the fatty acids

probably form a mechanical protecting envelope for the colour lake, and thereby increase its fastness and lustre.

Tannic acid also plays a part in Turkey-red dyeing, since without this acid it is impossible to produce a fast Turkey-red. Its chief action is to render the dye fast to chemicking (chlorine), a matter of importance in the case of yarns that have to be woven with unbleached yarn, and then fully bleached in the piece. As in the case of the fatty acids, here also it must be assumed that the tannic acid first fixes the alumina; whether, however, it is chemically combined with the Turkey-red lake or not is unknown.

Finally, so far as the composition of the "old red" is concerned, we must assume it to correspond in the main with that of the "new red." Fatty acid compounds of the alkalis are brought upon the fibre in large quantity, and are probably oxidised into oxy-fatty acid compounds. Hence, in the subsequent mordanting with alum, there must be formed the oxy-fatty acid compounds of alumina and alkali sulphate. Moreover, old red contains a larger quantity of oxy-fatty acid compounds with alkali, as such, a circumstance explaining the greater fastness of this dye towards acids, as also the softness of the dyed yarns and the readiness with which they can be moistened.

To produce this old red, the yarn is cleansed by steeping for some time in water, followed by boiling in soda, almost without pressure, and washing. Next follows the characteristic feature of the process—mordanting with oil. For this purpose the yarn is treated for about a minute with an emulsion of "tournant oil" and soda or potash, by the aid of a mechanical appliance imitative of hand-steeping, after which it is squeezed and dried. The first stage of drying consists in hanging the yarn on a series of wooden frames set up in a spacious courtyard; and from these frames the yarn is transferred to the drying chambers, where it is left for some time, *e.g.* overnight, exposed to a temperature of about 40–50° C. This temperature must not be exceeded, and for this reason provision is made in large works for the automatic ringing of an electric bell when an undue elevation of temperature occurs. When dry, the yarn must be perfectly cool before it is laid in heaps, otherwise it may be weakened as a consequence of over-heating.

This process of impregnation with oil and alkali is repeated three to five times. In the oil bath a dissociation of the oil into glycerine and the fatty acid compound of the alkali used takes place, the latter compound being absorbed by the fibre; so that the more often the bath is used the more glycerine will it contain. The absorbed alkali-fatty-acid compound is converted into an insoluble form when dried, probably by oxidation into an oxy-fatty acid

salt. The unmodified fat is finally washed out by treating the fibre with lukewarm water and a little soda, the resulting solution of soap being afterwards used as a brightening bath.

After oiling comes the sumach treatment, the yarn being steeped for several hours in a warm decoction of sumach leaves (12–13 per cent.); this is followed by squeezing and aluming, without any intermediate washing. The alum bath consists of a fairly strong (about 12 per cent.) solution of iron-free alum, neutralised as nearly as possible with soda. The yarn is stretched on rods and immersed in the warm liquor. The rods carry toothed wheels on their extremities, which wheels, by engaging one in another, set the rods in rotary motion, and thus enable the yarn to be reeled in the mordant liquor. When properly impregnated in this way, the yarn is left at rest in the liquor for several hours, after which it is washed, preferably with hard water (to neutralise the sulphuric acid in the bath), and is then ready for dyeing.

This operation is performed in wooden vats containing alizarine (mostly with blue tinge), a little sumach, and ox blood; and, in the event of the water being soft, a little calcium acetate must be added as well. The tannic acid and yellow pigmentary matter of the sumach are absorbed first by the fibre, and help to ensure regularity of dyeing. The addition of ox blood to the bath assists in clarifying the colour, the impurities being enveloped by the coagulating albumin of the blood, and thus kept from absorption by the fibre.

The yarn, stretched on frames, is immersed in the cold bath, which is then raised to 100° C. in three-quarters of an hour, the goods being well worked the while. They are then lifted, tied together, and immersed in the bath once more, where they are boiled for a further three-quarters of an hour, in order to completely fix the dye.

To brighten the colour the goods, after dyeing, are first boiled with soda in large vessels, under a pressure of about a quarter of an atmosphere, to remove all impurities. This is followed by a similar boiling with soap; though sometimes the yarn is passed through a cold solution of the salt before boiling with soap, this treatment giving a brighter red. It is assumed that the tin is contained in the form of tin oleate in the fibre. Finally the goods are well washed.

With the single exception of cost, this old red is superior in all its properties to the new red described below. The ratio of cost is as five to three. The fastness to acid and chlorine is greater than that of new red, and the yarn is also far softer. Yarns may also be dyed pink by the old red process.

The chief rôle played by the new red process is in the dyeing of piece goods.[1] The operations in this new method, which owes origin to the discovery of Turkey-red oil, are as follows: padding with the mordant, oxidising, dyeing, dunging, oiling, steaming, soaping, and washing. The first operations, which are performed in order to fix the alumina on the fibre, have already been described in the chapter on mordants, and will therefore be taken as known. The dyeing is effected in the hank, the usual adjuncts to the bath being sumach, bran, size, Turkey-red oil, and, in the case of soft water, calcium acetate. So far as the size is concerned, this adjunct is only employed as a resist, *i.e.* to protect from the dye those parts of the printed surface that are to finally appear white. The Turkey-red oil, having no particular influence on the colour, may be omitted with advantage, though still used in some works. The bran has a cleansing action on the colour lake, and the sumach plays the same favourable part here as in the old red process, both as regards the fixing of the alumina and the uniform absorption of the alizarine; however, as it stains the material yellow, it must be replaced by tannin when the production of a blue-tinged red is in question. Finally, so far as the alizarine itself is concerned, the marks mostly in use are those largely consisting of anthrapurpurine. The selection of the particular mark of alizarine to produce a given shade is facilitated by making small trial dyeings with so-called "garancin strips," *i.e.* strips of cotton fabric printed with alumina and iron mordants (these are obtainable from, *inter alia*, Koechlin Frères, Mülhausen). The amount of alizarine required depends on the thickness of the cloth and the depth of red to be produced; from $8\frac{1}{4}$ to $8\frac{3}{4}$ grms. of 20 per cent. alizarine being taken per yard of 30-inch material. Bran and sumach are used in equal parts—each one-half of the quantity of alizarine employed.

Greater care is needed in dyeing than with the old red process. The pieces are entered in the cold bath for half an hour, the bath then heated very slowly to 60° C., whereupon the steam is shut off and the dyeing proceeds in the cooling bath, so that the operation takes two to two and a half hours altogether; then follow washing and drying at a moderate warmth. In consequence of the presence of free calcium alizarate in the colour lake, the goods have a dirty brown look at this stage. Next follows padding with Turkey-red oil solution, the stronger the better for the beauty of the colour,

[1] According to Hummel, cottons are also dyed Turkey-red by the Steiner process, which consists in padding them in a hot oil bath, followed by quick drying at sharp heat, then padding with soda solution and drying as before, these two operations being repeated some seven times. The goods are next passed through soda and water, washed, dried, mordanted, dyed and brightened.

though this oil imparts a yellow tinge, which must be borne in mind when a bluish cast of red is desired. To give one example of quantities, 100 parts, by weight, of Turkey-red oil (90 per cent.) are taken per 1000 parts of water. For red that is to be afterwards discharged a smaller proportion of oil is taken, in order to facilitate discharging. After oiling, the goods are dried and then steamed, it being noted that the red comes out brighter when the stuff is introduced in a slightly damp condition into the steaming chamber.

Steaming is performed for two to two and a half hours under a pressure of about two atmospheres, and exercises a very beneficial effect on the brightness of the colour. It is succeeded by the equally important operation of soaping, which renders the colour purer and more vivid, the process being effected at boiling-heat for one and a half to two hours, with about half a pound of Marseilles soap per sixty-yards piece of cloth. To improve the brilliance of the colour and give it a yellow cast a little sodium stannate is added to the soap bath, the same procedure being adopted when the shade comes out too full.

As an appendix to the foregoing description, it must be added that the oiling process depends on the tinge—bluish or yellowish—to be developed in the red. In the former event a slight oiling is given, this taking place after dyeing; whereas in the other case a twofold oiling is applied—one before mordanting, the other after dyeing. For the first oiling, a strong solution—*e.g.* 25 parts, by weight, of Turkey-red oil per 100 of water—is used, the goods being padded with this and then dried; then mordanted as usual, fixed, dyed, and padded again, this time with a weaker solution—*e.g.* 6 per cent. of Turkey-red oil. If oil has been brought on the fibre before dyeing, this latter operation can at once be proceeded with, and at a higher temperature than that already given. In this event the reaction that, under ordinary circumstances, goes on in the steaming chamber is in part completed in the dye-bath.

Of late a very considerable improvement has been made in this new red process by abbreviating the cumbrous operation of mordanting. This improvement was based on the fact, already utilised in the old red method, that cotton containing a large proportion of oil can be mordanted with alumina by simple immersion in a solution of basic alum. The *modus operandi* is as follows:—The goods are padded with a strong solution (20 per cent.) of Turkey-red oil, then dried in the hot flue, immersed for some time in a solution of basic alum, squeezed, piled in heaps, and finally washed with hard water, or, preferably, entered beforehand in a warm chalk bath to neutralise the sulphuric acid from the mordant. All the subsequent

operations are performed as before. Yarns are also dyed new red in this manner.

The method of Schlieper and Baum effects the dyeing of Turkey-red in a very peculiar manner. The goods are first mordanted with sodium aluminate, and then treated several times over with chalk, in order to convert the sodium aluminate into calcium aluminate on the fibre. The dyeing is performed by passing the material through a boiling-hot solution of alizarine in lime-water, in three to four minutes. After dyeing, the goods are padded with "acid soap," dried, steamed, and soaped.

Although the red obtained by this method is cheaper than that from the ordinary process, the method itself has not met with any extensive application, probably because some of the details of the manufacture are known only in the inventors' own factory.

Mention should also be made of the Erban-Specht process, which is specially adapted for the production of pink. The details of the process are given in the prospectus issued by the Hoechst Farbwerke.

Colours in Competition with Turkey-Red.—Until lately alizarine was without a rival as a red dye for cotton, merely a few, quite fugitive, yarn-dyeings having been performed with croceine scarlet. However, since the discovery of Congo-red and benzo-purpurine, large quantities of cotton have been dyed with these in (fugitive) imitation of Turkey-red.

The most dangerous competitor of the last-named dye is nitraniline red, which has largely displaced alizarine in the dyeing of piece goods, mainly by reason of its greater cheapness, the ratio of the cost of production of the two dyeings being about 4 : 1. Moreover, nitraniline red has the advantage of dyeing the goods through better than its rival, which remains more on the surface, so that materials dyed with alizarine red are unsuitable for raising. On the other hand, nitraniline red has some very grave drawbacks, the colour being too crude and glaring, as well as less fast to light and the influence of weather than alizarine red, especially when produced without the aid of antimony. In addition, its covering power is low, on which account the goods require to be well bleached beforehand, whereas Turkey-red will satisfactorily mask even a yellow cotton.

Dyeing with Catechu.

Thanks to its great fastness, this natural dye-stuff still plays a very important part in cotton-dyeing, and would be even more largely used, especially in calico-printing, if it could be discharged.

It also deserves remembrance in wool-dyeing, at least in such cases where great fastness to light is in question.

Catechu dyeings have only one drawback, viz. that the material becomes harsh when dyed in dark shades.

The dyeing process is based in part on an oxidation whereby the colourless catechu is converted into brown japonic acid, and partly on the formation of a colour lake.

Light catechu shades are produced on loose cotton and yarns in the following manner:—The goods are dyed for a half to one hour at 60° C. with yellow or brown catechu, or a mixture of both, and an addition of about 2 per cent. of copper sulphate. They are then treated for about twenty minutes in a bath of potassium bichromate or iron pyrolignite—the former applied warm, the latter cold. Developing with chrome gives reddish brown shades, iron greenish tones, intermediate shades being obtained by mixing the developers.

Yellow shades are produced by adding fustic and alum to the dye-bath; for duller and more greyish tones the foregoing adjunct is replaced by logwood without alum.

Dark catechu dyeings are always produced by the aid of dye-wood extracts (logwood, fustic, redwood).

In dyeing loose cotton and yarn, the *modus operandi* is as follows:—The goods are boiled for about an hour and a half in the dye-bath, containing catechu and copper sulphate, eventually also logwood or fustic extract, and then lifted and left exposed to the air. On the following day they are treated in a hot bath of potassium bichromate, and afterwards in a hot bath containing varying quantities of different dye-wood extracts, according to the shade required. This final dye-bath occasionally receives an addition of alum, or also tin salt for reddish tones.

Piece goods are first padded with a weak acetic acid solution of catechu, and dried, then passed through a hot solution of potassium bichromate, partially neutralised with soda, rolled up, and left alone for some time. In the case of dark shades, the pieces are passed a second time through the chrome bath, and left rolled up for several hours. Yellower tones are obtained by adding alum to the chrome bath; still yellower shades by adding alum and fustic extract; whilst, for very dark shades, an addition of logwood extract is given.

Catechu dyeings are frequently shaded by the aid of basic dyes, applied in a fresh bath in association with alum.

More recently a product obtained by treating catechu with potassium bichromate or alum has been put on the market under the name of "prepared catechu" or "catechin."

Black-Dyeing Cotton with Logwood.

The employment of logwood in the black dyeing of cotton has suffered considerably from the competition of aniline black and various substantive dyes.

The first black on cotton was produced with sumach and iron mordants, the colour, however, being only a dark grey. At present there are two chief methods of dyeing cotton black with logwood. The first of these, which is mainly employed for loose cotton and yarn, consists in producing a colour lake from logwood, tannic acid, and salts of iron and copper, in various ways.

The most rational of these is the following:—The cotton is first left overnight immersed in a decoction of 40 per cent. of sumach; it is then squeezed and treated for half an hour in a cold solution of iron pyrolignite (of about 3° B. density), followed by passing it through very dilute lime-water, and thoroughly washing. By this means iron tannate is produced on the fibre; the lime treatment serves to neutralise the acid. The iron pyrolignite may be replaced by "iron nitrate" or ferrous sulphate, a little levigated chalk being added to the bath in the latter case. A handsomer black is obtained by the use of alumina mordants—a little aluminium pyrolignite, for example, being added to the iron bath.

The cotton thus prepared is next dyed with logwood, sometimes in presence of a little fustic, by entering in the cold bath, which is then slowly raised to boiling. To increase the fastness of the black, the stuff may afterwards be treated in a bath of bichromate ($\frac{1}{2}$ part per 1000, at 60° C.) or iron nitrate. Sometimes the shade is darkened in the dye-bath itself by an addition of copper sulphate.

Finally the cotton is soaped, a treatment that makes the tone of the black more agreeable.

The numerous variations of this method have been described by Ed. Weiler (Lehne's *Färber Zeitung*, 1889–90, p. 137).

The following method is generally employed for the production of mourning goods in piece dyeing:—The stuff is padded with a mordant solution consisting of 3 parts of iron pyrolignite (6° B.) and 7 parts of aluminium pyrolignite (7° B.), then fixed and dyed in a bath containing, in addition to the necessary quantity of logwood and a little quercitron, $2\frac{1}{2}$ oz. of borax, $1\frac{1}{4}$ lb. of sumach, and $5\frac{1}{2}$–$6\frac{1}{2}$ lb. of cow dung, per 22 gals. of bath liquor. For the first quarter of an hour the bath is cold, after which time it is heated so as to bring the temperature up to 80–90° C. in about an hour. After dyeing, the goods are washed, treated with bran, and washed again. The bran bath is prepared by boiling bran—packed

in close bags—in water, in the proportion of 1 part, by weight, to 100 parts of water, the cotton being then treated in this hot liquor for twenty minutes.

5. Application of the Vat Dyes.

This group contains only two dye-stuffs—indigo and indophenol blue. Both are insoluble in water, and therefore cannot be used directly for dyeing. On the other hand, their leuco-compounds are soluble, have a very decided affinity for the fibre, and are also gifted with the property of being readily reconverted into the dyes themselves under the influence of weak oxidising agents. Consequently, in order to dye with these dye-stuffs, all that is necessary is to impregnate the fibre with the reduced dye in solution, and then expose it to the air. The fibre absorbs the leuco-compound of the dye-stuff, which is then reconverted by the atmospheric oxygen into the corresponding insoluble dye, the latter being precipitated firmly in and upon the fibre.

This method has been practised from time immemorial with indigo, and plays a highly important part, inasmuch as indigo has been, and still is, the chief vat dye-stuff known.

"Vat dyeing," or "blue dyeing," is the term usually applied to dyeing with indigo, since, with the exception of the comparatively unimportant indigophenol, no other dye is applied in this manner, nor can indigo itself be fixed on the fibre in any other way.

The term "vat" applies to the vessel employed for dissolving the indigo, and also to the solution itself. This latter is prepared by the aid of various reducing agents, which, however, can only be used in presence of an alkali, the resulting indigo white being insoluble except in alkalis.

The vats may be divided into warm and cold, or fermenting and non-fermenting, vats. To the fermenting vats belong the woad, soda, potash, and urine vats; they are warm vats, and are employed exclusively for wool. The non-fermenting vats comprise the zinc or preparing vat, the vitriol vat, the hyposulphite vat, and the indigo-indigophenol vat. The first two of these are cold vats, and are therefore used solely for vegetable fibres; the others are warm vats, and can be applied to the dyeing of both vegetable and animal fibres.

Whichever vat be employed, the first task is essentially the careful comminution of the indigo, since it is only when this substance is in a fine state of division that it can be brought into solution by reducing agents. For this purpose the indigo is mixed into paste with water and alkali, and ground for some consider-

able time in an indigo mill, of which there are numerous types.

The most important of the fermentation vats is the woad vat, which plays a principal part in the dyeing of wool, and is used solely for this purpose, the warm vats as a whole being ill adapted for dyeing vegetable fibres, whilst the application of indigo to silk-dyeing has now been abandoned.

The fermenting materials used in the preparation of the woad vat are woad, madder, bran, and syrup, the woad playing the chief part in the mixture. The addition of madder is in so far favourable that, apart from its fermentative action, this substance takes part in the dyeing process by virtue of its tinctorial character, a valuable consideration when dark shades are in question. The bran acts as an instigator of fermentation, and, in addition, imparts to the bath liquor a certain degree of viscidity favourable to the suspension of the indigo that is to be dissolved therein. However, since the presence of a large quantity of bran would tend to choke the vat, a portion of this substance is replaced by syrup.

The alkaline adjuncts to this vat are lime and soda. They serve to neutralise the acidity engendered by the fermentation, and to maintain the liquor in the state of alkalinity essential for bringing the indigo white into solution. In addition, they retard fermentation, and therefore afford a means of regulating the progress of this operation.

The woad vats are usually round in shape, measuring about eighty inches across and eight feet in depth, and are set about two-thirds in the ground; for yarn-dyeing they are mostly square.

The vats are started by powdering the woad, mixing it into a paste with boiling water and leaving to stand for some time, after which it is introduced into the vat, filled with water, the madder, bran, lime, soda, and ground indigo being then added. The proportions employed are—woad, 220–330 lb.; indigo, 11 lb.; madder, 33 lb.; bran, 33 lb.; lime, $4\frac{1}{2}$ lb.; soda, 22 lb. The vat is now heated to 100° C., stirred up well, and covered up, after the fire has been drawn, in order to keep warm as long as possible—an essential condition for the inception of fermentation. After standing twenty-four hours the vat is uncovered to see whether fermentation has begun, which will be the case if the liquor "works," *i.e.* throws up a number of small bubbles; whilst the initially blue colour of the liquid has now become a yellowish green, a blue scum floats on the surface, and the smell has changed. Should these indications be absent, the vat is covered up again and left to itself for some time longer before being reinspected. As a rule, the woad

vat will have begun to ferment in two to three days, though the actual time may vary according to the time of year.

When fermentation has commenced, the vat is limed by adding finely sifted slaked lime at intervals of two to three hours, stirring the contents up well after each addition. By this means the acidity produced during the fermentation is neutralised, and the fermentation restrained at the same stage for some time, in order to bring the whole of the indigo into solution. The newly started vat cannot be used for dyeing immediately, because at this stage the fermentation and the solution of the indigo are only just begun; in fact, the vat is not fit for use until it has been limed several times and a large proportion of the indigo has been brought into solution. The vat in this stage exhibits the following characteristic indications:—The vat liquor is olive green in colour, and carries on its surface a layer of copper-blue scum, the "bloom," $\frac{1}{2}$—1 inch deep; the smell is peculiar and faintly ammoniacal; and, where the separated scum has left the surface visible, a number of blue "veins" appear. When the vat has arrived at this stage, it must be used at once for dyeing, and not left any longer, otherwise the fermentation will proceed at the expense of the indigo. The woad vat can be kept in use for several months in succession, provided it be maintained in good condition in the following manner, the process, however, being one of the most difficult tasks the dyer has to perform:—After dyeing a whole day, the vat is reinforced in the evening by the addition of a certain quantity of madder, syrup, and lime, then heated, well stirred up, and left covered up all night for use the following day. In order to replace the loss of indigo sustained in dyeing, an addition of this dye-stuff must also be made at intervals every day or second day.

The two extremes to be avoided are excessive fermentation owing to an insufficiency of lime, and a cessation of fermentation through an excess of that adjunct. The former condition, known as mildness, because of the sweetish odour evolved, can be remedied by adding lime at intervals until the smell and appearance resume their normal condition. If, on the other hand, the vat contain too much lime, it is considered to be sharp, and will smell strongly of ammonia, in which event the excess of lime must be neutralised by a gradual addition of acid, the fermentation being restarted by the aid of bran. Unless excessive fermentation be checked in time by adding lime, the colour will be wasted; and the final condition of a sharp vat is blackening. In either event, it is often impossible to remedy the defect, and the liquor has to be run to waste. This can, however, be avoided by careful supervision; the dyer must be able at any time to tell, from the appearance, smell, and behaviour

during dyeing, whether the vat needs an addition of lime or a ferment.

Vat-dyeing is performed at a medium temperature (about 50° C.), and in this case, more than any other method of dyeing, great care is necessary to see that the goods are thoroughly damped beforehand. The scum must be removed before entering the goods. Loose wool is invariably dyed in circular vats, the wool being enclosed in a net, completely immersed in the vat liquor, and worked about therein by means of sticks. After about an hour it is lifted and well squeezed to express the excess of liquor. At this stage the colour is green and has to be developed into blue by oxidation, for which purpose the wool is thrown in a heap on the floor and shovelled over so as to expose all parts to the air. If the vat is in good condition the lifted wool will have a yellowish green shade, which afterwards turns dark green before arriving at the blue stage, the latter being attained gradually. If the change occurs too quickly, the vat is too sharp; and converse behaviour indicates excessive mildness, the condition of the bath being thus determinable by dyeing a small sample and observing its behaviour after lifting. Occasionally such parts of the wool as have not come in contact with the air remain quite white. The development of the blue will be complete in about a quarter of an hour, whereupon the wool can be re-entered in the vat if a darker shade is required.

To produce a bright light blue, a fairly fresh vat is essential, and this must contain less lime, and consequently more soda, than usual. However, the vat should not be quite fresh, since the first parcel dyed in the vat is always dull and muddy in colour, in consequence of the dun-coloured pigments of the madder and the woad. Finally, this vat must be rather weak in indigo.

To match a dark blue exactly to pattern, the goods must first be blued in a strong vat until the desired shade is nearly attained, and then finished in a weak vat.

Yarns are suspended on smooth sticks, then immersed in the vat liquor, and kept well worked about therein, after which they are lifted, squeezed, and left to blue.

For piece dyeing, the vat is fitted with an attachment which enables the goods to be kept in motion all the time and below the surface of the liquor. At the end of one to three hours, according to the strength of the vat and the depth of colour to be produced, the pieces are unwound and the superfluous liquor squeezed out between rollers. To develop the colour the pieces are alternately folded and opened out, and are finally washed. Vatted pieces must not be left for any length of time in a warm place before washing, or they will be liable to turn mouldy.

The other fermentation vats are managed and applied in the same way as the woad vat, but, as they are of little practical importance, no further description is necessary.

Frequently, in order to save indigo, vatted goods are topped with logwood, for which purpose they are first mordanted with alum, copper sulphate, potassium bitartrate, and oxalic acid, and then dyed with logwood. In other cases, however, they are mordanted in the same manner as for logwood blue (*q.v.*), which is a decided irrational process, the greater part of the indigo on the fibre being destroyed by boiling in the bichromate bath. These dyeings are known as "semi-fast blue," being less fast to light than vat blue.

Occasionally the topping with logwood is only intended to secure better equalisation of the dye, uniformity being difficult to obtain on piece goods in vat dyeing.

To produce a semi-fast blue with a blackish appearance, which though less brilliant than, is quite as fast to light as, true vat blue, and is also fast to wear, the goods are first blued in the vat, then boiled with santal, and afterwards vatted anew.

To impart a vivid appearance to vatted piece goods, they may be topped with a small quantity of methyl violet or archil.

The Hyposulphite Vat.—This vat is dealt with in connection with the fermentation vats, inasmuch as it also is used warm and is chiefly employed in wool-dyeing.

The hyposulphite vat is based on the property of the hydrothionic acid discovered by Schützenberger, of forming with indigo a colourless double compound, which is soluble in alkalis and is decomposed by the weakest oxidising agents, indigo blue being thereby liberated. For practical use, the sodium salt of hydrothionic acid is prepared by allowing zinc dust to act on the bisulphite in a tightly closed vessel, the mixture being kept stirred and cooled. The reaction is complete within about an hour, and is probably well expressed by the following equation:—

$$4NaHSO_3 + Zn = Na_2S_2O_4 + Na_2SO_3 + ZnSO_3 + 2H_2O.$$

The hyposulphite solution is rendered slightly alkaline with milk of lime, in order to diminish its instability, and is then ready for use. It is preferably stored under a gas seal. A stock solution of indigo is then prepared by heating 1 part of ground purified strong indigo with 4 parts of hyposulphite to 80° C. for some little time. Of the resulting yellow-brown solution, a definite quantity, depending on the depth of blue desired, is added to the vat along with hyposulphite.

Wool is dyed in the hyposulphite vat at 50–60° C., a temper-

ature that must not be exceeded by more than a few degrees. At the outset the vat liquor will be bluish grey in colour, and does not dye so well as when it has changed to yellowish green; in fact, in this first stage it behaves like a sharp woad vat.

In worsted dyeing, the hyposulphite vat plays the most important part in the production of light shades that cannot be obtained in the same degree of beauty by means of the fermentation vats; consequently this method of application will be described first.

The vat, filled with hot water, is first charged with the necessary quantity of stock solution and commercial hyposulphite solution at the rate of about 3 gals. per 1100 gals. of vat liquor; after being well stirred up the vat is ready for dyeing. In the case of very light shades, the principal consideration is perfect equalisation, and this depends on two circumstances—(1) the well-damped yarn must be carefully separated into individual hanks, each of which is then suspended from a separate very smooth hazel rod; (2) the conversion of the green dyeing into blue must be performed in the most careful manner possible, as described in detail below. If these conditions are not properly fulfilled, the colours will be uneven and mixed.

The rods laden with yarn are set side by side in a wooden frame, without touching one another, the whole being then slowly dipped into the vat. Here they are turned by hand at intervals, and remain until it is quite certain that the absorption of dye has ceased. This is necessary, because the hanks cannot be all taken out at the same time, but must be lifted in succession; and, since it is essential that the whole parcel should be uniform in depth of colour, no opportunity can be allowed for any of the hanks to absorb more dye than the rest.

The absorption will be complete in about half an hour, whereupon the hanks are lifted from the vat one after another, rapidly squeezed, and then rinsed in cold water in the following manner:—Three or four tanks, about 10 feet long by 40 inches wide, are placed in a row close by the vat, and through these the yarn is passed in succession, being opened by a pair of workers in the first tank, worked round, taken over, and treated in a similar way by a second pair of workers, and thereby advanced a stage, the operations being repeated until the end of the last tank in the row is reached, whereupon the yarn is squeezed and drained in the hydro-extractor.

The object of this treatment is to remove the superfluous vat liquor from the yarn as quickly as possible, and enable the blueing process to proceed gradually. The water in the said tanks must be renewed at intervals during the progress of the work; this applies particularly to the first tank, since this receives the largest

quantity of vat liquor. The changing can be effected by making the feed and discharge continuous.

The colour of the freshly lifted yarn is yellow, changing to green in the first rinsing tank, and then gradually turning blue, the change not being quite complete till the yarn has passed through the hydro-extractor.

In this manner the palest blue shades can be obtained in perfect uniformity and clearness, the possibility of which forms the chief advantage of the hyposulphite vat.

Before dyeing a second parcel of yarn in the once-used vat, the latter is replenished with indigo solution and hyposulphite (about 1·32 gal. of this last per 1100 gals. of vat liquor).

In dyeing dark shades the proportion of indigo solution and hyposulphite must be increased, *e.g.* for 6·6 lb. of indigo $5\frac{1}{2}$ gals. of hyposulphite. After dyeing for about half a day, a further quantity of about $3\frac{1}{2}$ gals. of hyposulphite must be added.

For dyeing piece goods the vat is fitted with an appliance for keeping the pieces in motion, as in the case of the woad vat, and, after dyeing, the pieces are conveyed to the rinsing tanks over a set of guide rollers. Loose wool is dyed as in the woad vat.

About 4 cwt. of wool per diem can be dyed medium blue in a hyposulphite vat measuring 10 feet in depth and $6\frac{1}{2}$ feet in diameter.

Quite a dark blue can be easily and quickly produced in the vat by an addition of acetic acid, it being unnecessary for the vat liquor to be strong. However, the dye-bath in this case cannot be used again.

In addition to the already quoted advantages of the hyposulphite vat come the following, which render it the most perfect vat for wool-dyeing:—Easy manipulation; non-necessity for supervision, since it may be laid aside to rest at any time; can be used for dyeing as soon as set; no sediment is formed except the dirt deposited by the wool; the resulting blue is perfectly fast to washing —at least in light shades—and does not rub off.

On the other hand, the hyposulphite vat is very little used for cotton-dyeing, and then only at low temperatures—about 25–30° C.

What the woad vat is for wool, the zinc vat is for cotton and linen. It has for the most part displaced the old vitriol vat, and is now almost the only vat used for cotton-dyeing. Its action is based on the property possessed by zinc dust, of readily decomposing water in presence of an alkali, and combining with the liberated oxygen, whilst the hydrogen reduces the indigo blue to indigo white, which is immediately dissolved by the alkali—

$$Zn + 2H_2O = Zn(OH)_2 + H_2.$$

Lime is the alkali generally used here.

A stock vat is first set by mixing together 10 parts of ground indigo, 7 parts of zinc dust, and 20 parts of lime, to form a pulp with water and leaving the whole to ferment in a tub. In about twenty-four hours the process of reduction will be complete, whereupon a portion of the contents of the stock vat is transferred to the dye vat, stirred up in the cold water with which the latter is filled, and left at rest until the liquor has clarified, by which time the vat will be fit for use. The zinc vat varies in size and shape, but in the usual round form the ratio between depth and diameter is about $2\frac{1}{2} : 1$.

The appearance of the zinc vat differs little from that of the woad vat, whilst the management is much easier, all that is necessary being an occasional replenishing from the stock vat or an addition of zinc dust or lime. If the vat liquor be green, too much indigo is present; if yellow, too little. When there is a deficiency of lime the vat becomes turbid through the evolution of hydrogen. After

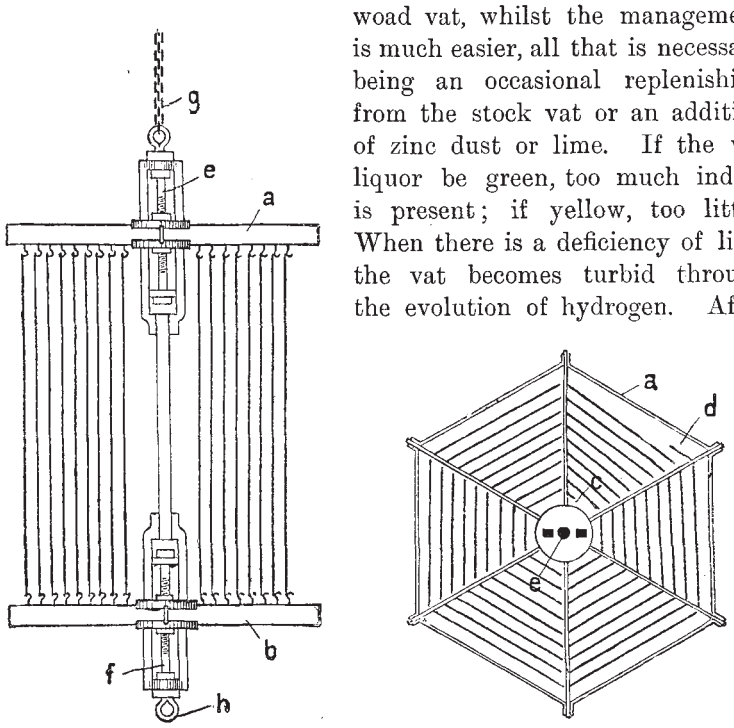

FIG. 26.

each addition to the vat the liquor must be stirred up and then left to settle before use.

Cotton may be dyed in this vat in all stages of manufacture; most frequently in piece form, less often as yarn. The piece of cloth to be dyed is wound on the frame shown in Fig. 26 in such a manner as to preclude contact between any two adjacent layers; and, after the scum has been removed from the vat, the frame is immersed in the liquor and kept therein for five to ten minutes. The frame is then lifted and kept in the air for an equal time, in

order to develop the colour. If the goods be dyed in several dips, the frame must be reversed after each, or else the lower part of the cloth will come out darker than the rest. After dyeing follows "souring," which consists in entering the cloth, full width, in sulphuric acid of about 2° B. density, to remove adherent calcium carbonate and consequently brighten the colour. The operation is completed by washing. The indigo dissolved in the processes of souring and washing must be recovered.

If the blue be desired to have a coppery appearance, the goods must be dried by heat. The brilliancy of the colour may be improved by methylene blue and methyl violet, these being, however, applied in the dressing, and not in the dyeing process.

Frequently, and especially in yarn-dyeing, the operation of vatting is preceded by a bottoming with some other dye. This is primarily intended to economise indigo, but the goods are also dyed through better, and sometimes also the tendency of the vat blue to rub off is diminished by this means. The dyes used for this purpose are Columbia-black R, diamine black, Chicago-blue, benzo blue-black, etc. In small dyeworks topping with logwood is often practised, the dyed cotton being treated in a bath of logwood, alum, and copper sulphate, or else first entered in a solution of iron pyrolignite and then dyed with logwood and alum.

Finally, it may be mentioned that the dyed yarns are often treated in a hot chalk bath, which diminishes the tendency of the colour to rub off.

The most important improvement in piece dyeing was the introduction of the continuous vat, a process wherein the alternate dipping and lifting of the goods is effected in a continuous manner by leading the cloth upwards and downwards over a series of rollers, partly in and partly out of the vat. The roulette vat is a kind of double vat, the dyeing process corresponding to a double passage through the continuous vat.

The continuous vat process is superior to the older method in every respect; the blue is handsomer and better fixed; less indigo is lost in the washing, and, owing to the pressure of the squeezing rollers, the goods are dyed through better and a better green is obtained; moreover, there are fewer light patches, and even dead cotton is dyed. For discharge effects this vat alone is employed, on account of the necessity for having a handsomer blue than is required when the goods are of one colour throughout.

The vitriol vat is set with indigo, ferrous sulphate, and lime; the management and application are the same as for the zinc vat. Over the latter it possesses a single, but not unimportant, advantage, namely, that the blue is fixed better, owing to the slower rate of

dyeing. In all other respects it is inferior to the zinc vat, so that nowadays it is but seldom used.

The indigo-indigophenol vat is set in a similar manner to the hyposulphite vat. Its advantage consists in replacing a portion of the indigo by the cheaper indigophenol. It is, however, not very easy to manage, owing to the difficulty in regulating the addition of hyposulphite, and has not attained any practical importance.

Dyes competing with Indigo.—Attempts have been made to supersede indigo, for wool-dyeing, by a number of blue mordant dyes, such as alizarine blue, anthracene blue, alizarine cyanine, brilliant alizarine cyanine, etc., with some degree of success; and at the present time a number of dyeings that were formerly performed with indigo exclusively are carried out with these substitutes.

The superiority of indigo over these rivals consists in the handsomer and fuller appearance, conjoined with the unsurpassed fastness of the colours to light. True, indigo fades a little under the influence of light; nevertheless, the blue, even in the lightest shades, always retains its handsome, bright tone, which is not the case with the other dyes mentioned. In fact, the latter can only replace indigo for dark shades, leaving it unrivalled for light blues, especially since the introduction of the hyposulphite vat.

A dye largely used of late is Bayer's sulphocyanine, by reason of its excellent fastness to wear and resemblance to indigo in colour.

For cotton-dyeing a number of basic dyes, such as indoine, naphtindone, diazine blue, new blue, indamine blue, indophenine, meta- and paraphenylene blue, etc., have been employed to imitate indigo. However, when subjected to test, the resulting dyeings are far inferior in fastness to indigo, and the superiority of the latter becomes still more apparent. Under the action of acids, bleaching powder, washing, and light, indigo dyeings suffer merely quantitative alteration, the brilliant blue colour remaining unchanged. The rival dyes, on the other hand, mostly become discoloured, often reddish grey, and, in the dark shades, mostly rub off quite as much as vat dyeings. The best of these substitutes is indoine blue (B.A.S.F.) which is identical with naphtindone (C.) and diazine blue (Kalle).

Dianisidine blue is incapable of replacing indigo for piece cottons, on account of its deficient fastness to acid; and, moreover, this dye is difficult to equalise. On the other hand, the developed or coppered dyeings of certain of the substantive dye-stuffs, such as diaminogen (C.), diazo blue R (By.), diamine blue RW (C.), etc., which are very fast to light and washing, give promise of becoming useful substitutes for indigo.

Other dyes largely used for the production of dark indigo blue

dyeings are various kinds of diamine black, either direct dyed or developed, as well as direct-dyed diazo black and diamine blue BX.

6. Application of the Developing Dyes.

The developing dyes are not purchasable in the finished condition, but are produced on the fibre. They are applied solely to cotton, and are distinguished by their fastness. They are divided into three groups—(1) the ice colours; (2) aniline black; (3) mineral dyeings.

Before proceeding to a special description, the following observations should be made:—The first stage in the production of these dyeings on piece goods consists in bringing the dissolved potential dye-stuff upon the fibre by padding, squeezing, and drying. In performing these operations it must always be borne in mind that the amount of the substance thus brought on the fibre depends not only on the strength of the solution, but also on the pressure of the squeezing rollers employed, which must therefore receive particular attention.

The name "ice colours" is applied to a series of insoluble azo dyes, which are produced on the fibre, from their components, by the aid of ice as a cooling agent. The first processes of this kind were those described in the patents of Read, Holliday, & Sons, of Huddersfield (1880), and Fr. Grässler. Great difficulties had, however, to be overcome in applying the method on a large scale, and it was not until the end of the eighties that J. J. Weber, of Winterthur, succeeded in producing a red from amidoazobenzol and β-naphthol on the fibre, on a manufacturing scale. Credit is also due to the Hoechst Farbwerke in particular, in connection with the further extension of these dyes, which, thanks to their cheapness and beauty, now play a very important part.

The method actually practised is briefly as follows:—The well-bleached cotton pieces are padded with a solution of β-naphthol in caustic soda, then dried, and afterwards passed through a solution of a diazotised amine, cooled by means of ice. The chief dyeings are—

Scarlet with ρ-nitraniline;
Bordeaux „ α-naphthylamine;
Brown „ benzidine sulphate, with or without addition of α-naphthylamine;
Blue „ dianisidine.

In addition, for reds, there are azophore red, nitrosamine red, phenetidine red, and, for a yellowish Turkey-red, β-naphthylamine;

for blue, azophore blue; and for fast garnet, amidoazotoluol,—to be considered as amines. Moreover, blacks have latterly been produced by this process, use being made of "azo black base" (M.L.Br.), consisting of a mixture of dianisidine and benzidine; as well as azotol C (C.), either of which gives a black with β-naphthol; as also the combination of nitraniline and naphthol BD (C.).

The different manufacturers of dye-stuffs are busily endeavouring to increase the number of these dyes and to improve those already known. This applies particularly to nitraniline red and dianisidine blue, the endeavour being to produce the former in a more bluish tinge, similar to Turkey-red, whilst with dianisidine blue the endeavour is to improve its worst quality—the lack of fastness to perspiration.

For red shades, the solution of β-naphthol in caustic soda receives an addition of Turkey-red oil and sodium aluminate, or, in place of the latter, para soap PN; for blue, the adjuncts consist of ammonium ricinolate and sodium acetate, tragacanth being added in all other cases. The caustic soda employed for red must be *pure*, since this gives a dye less tinged with yellow and less liable to rub off. In the case of bluish reds, β-naphthol is replaced by naphthol R, and for blue to stand the influence of perspiration, naphthol D.

After the pieces have been padded with the preparation, they are dried, as thoroughly as possible, in the hot flue at a temperature of 60° C.; the better the drying, the fuller the resulting colour and the lower the tendency to rub off, though the use of high temperatures must be avoided or the naphthol will be vaporised. The goods cannot be treated with the preparation long in advance, but must be further treated as soon as possible afterwards—at any-rate during the same day,—or partial browning may ensue.

The stability of the preparation can also be improved by the addition of an antimony salt dissolved in glycerine (Lauber & Caberti's patent); and a preparation of this kind is met with in commerce under the name of naphthol LC. Probably other alkaline reducing agents would also have the same effect.

In preparing the diazo solution of the amine for the developing bath, the amine is generally dissolved in hot hydrochloric acid and water, then cooled with cold water and mixed with a solution of sodium nitrite, accompanied with lumps of ice. The nitrous acid of the sodium nitrite is liberated by the excess of hydrochloric acid, and converts the amine into the corresponding diazo compound. Ten minutes, or even longer in some cases, should be allowed for the completion of diazotisation; the liquid is then filtered, and the

hydrochloric acid, which would retard the coupling process, is neutralised by the addition of a cold solution of sodium acetate immediately before use.

In so far as the diazo solution contains an excess of free mineral acid, it is fairly stable, and can also be prepared without ice. After the addition of sodium acetate, however, it becomes readily decomposible.

For some browns, tragacanth is added to the developing bath; and for dianisidine blue a solution of copper chloride is added in addition to tragacanth and wheaten flour, the colour being thereby rendered greener and faster to light. According to the recipe of the Hoechst Farbwerke, chromic acid should be added as well, in order to improve the fastness to perspiration and brighten the colour.

To produce the azo dye on the fibre the fabric, prepared with naphthol, is passed more or less slowly through the developing bath, and then either led direct into water, or else carried through the air for some distance, in order to allow sufficient time for the completion of the coupling process, which varies with the different dyes; sometimes the goods must be left as long as a quarter of an hour before washing. The dianisidine and azophore blues furnish brighter colours, of more greenish tinge, when the development is performed in two baths, in which case the second bath contains only the sodium acetate required for neutralising the hydrochloric acid. A passage through the Mather and Platt apparatus is particularly desirable for the full development of these colours, this treatment also making them greener in shade and faster to perspiration.

The rapid oxidation apparatus of Mather and Platt, or, as it is generally termed for short, "the Mather and Platt," is a continuous steaming apparatus, and is largely used in calico-printing. In the view of this apparatus shown in Fig. 27, *a* is an iron case of circular or quadrangular section, through which the goods *i*, from *h*, are passed over stretching rods *k*, *l*, and guide rollers *n*, *o*, in an ascending and descending direction, by means of the two sets of rotating rollers *b*, b_1, and are finally discharged through the same aperture above the rollers *p*, *q*, to be laid on the table *x*, by the folding device *u*, *v*, *w*. The rate at which the goods are moved forward is usually regulated so that they remain in the apparatus about one minute.

Other details represented in the figure are—1, the steam admission valve; *y*, the perforated steam-pipe; *z*, a false bottom; 2, the waste steam valve; *g*, a small steam-engine; *h*, a belt pulley; *f*, a fly-wheel; and *d*, a belt pulley, with the speed gear *o*.

The copper pipes situated at the inlet and outlet aperture for

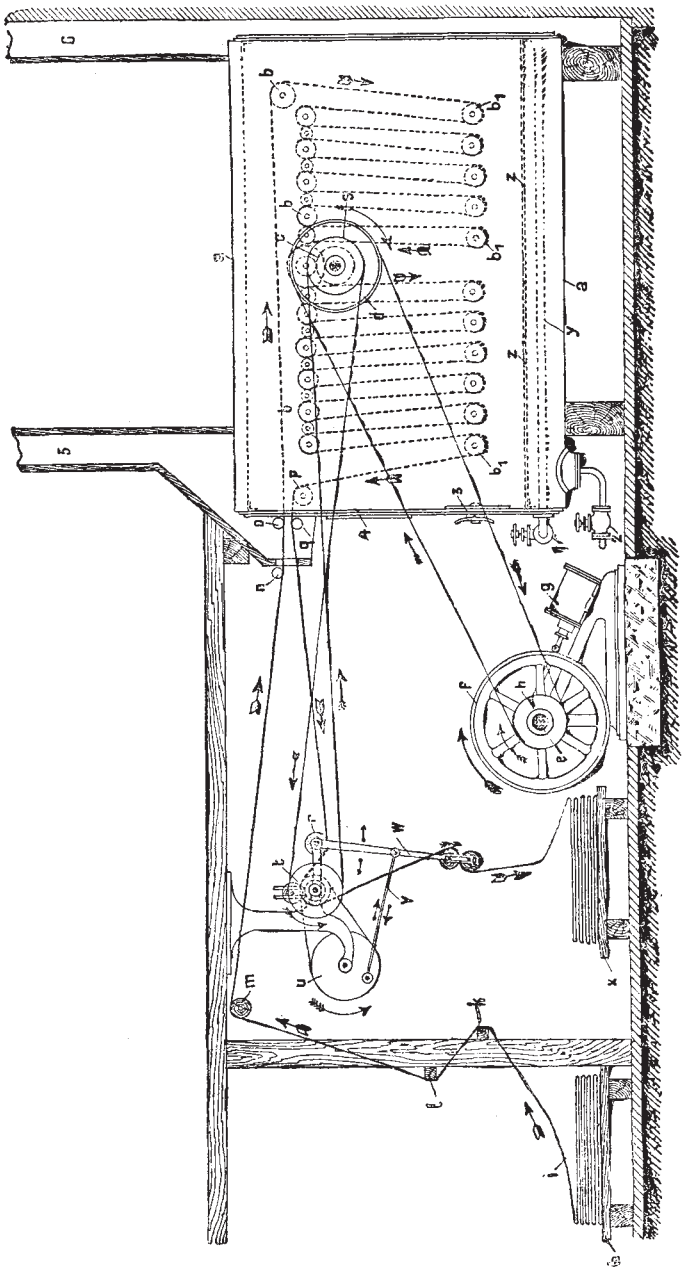

Fig. 27.

the goods are also heated with steam, to prevent wet stains arising from condensation.

The final operation in all these dyeings is a soaping at 60° C.;

in the case of reds an addition of soda is advisable at this stage, to give the colour a more bluish tinge.

The dyeing of nitrosamine red is performed in a somewhat different manner, by reason of its constitution, both the components being brought on the fibre at the same time by entering the goods in an alkaline solution of β-naphthol, nitrosamine, tragacanth, and Turkey-red oil. They are then immediately dried, and left for fourteen hours for the colour to develop.

Sundry practical difficulties are encountered in the dyeing of yarns with ice dyes, but these have mostly been overcome, especially in the case of nitraniline red.

Aniline black is the handsomest and fastest black for cotton, and has been the subject of more research and description than probably any other dye. It is applied to unbleached raw cotton, and can also be dyed on dressed cotton, the advantage of this latter process being that the colour is brighter through not being covered over by the dressing.

Aniline black is produced by the oxidation of an aniline salt in two different ways, and we therefore have oxidation black and single-bath aniline black. The former and older method was first applied to calico-printing and afterwards transferred to the dyeing industry. The material is padded with a solution containing an aniline salt and oxidising agent, sal ammoniac (as hygroscopic), and generally also a carrier of oxygen, after which it is dried, the black being then developed by warm hanging or steaming, chroming, and soaping. The aniline salt generally used is aniline chloride, which should be as pure and free from toluidine as possible. The quantity employed in practice varies very considerably, the average being about 100 parts, by weight, per 1000, although a useful quantity can be obtained with 80 parts. The oxidising agent consists of sodium- or potassium-chlorate or a mixture of the two. In the different recipes employed in practice the average ratio between the chlorate (reckoned as sodium chlorate) to the aniline chloride is as 0·4 : 1·0. The oxygen carrier employed is a solution of vanadium or precipitated copper sulphide. Vanadium can be replaced by cerium, which is said to give the finest black. The preparation may be made by dissociating the cheap mineral cerite with sulphuric acid. The vanadium solution is prepared by dissolving 20 grms. of commercial ammonium metavanadate in 100 c.c. of hydrochloric acid and 200 c.c. of water, warming along with commercial bisulphite until blue coloration and complete solution occur, and then diluting to 20 litres ($4\frac{1}{2}$ gals.). This solution will then contain 1 part per 1000, by weight, of ammonium vanadate as chlorate (H. Schmidt).

The copper sulphide is prepared as follows:—11 lb. of flowers of sulphur are well mixed with $4\frac{1}{2}$ gals. of 36° B. caustic soda and left for a few days until completely dissolved, gentle heat being applied if necessary; on the other hand, 53 lb. of copper sulphate are dissolved in 55 gals. of water and added to the above solution of sodium sulphide, the precipitate being collected on a flat linen filter and well washed with hot water. The precipitation should not be effected from a concentrated solution, or the sulphide will go down as coarse granules, enveloping a portion of the copper sulphate solution, which would then rapidly decompose the padding solution (Kielmeyer). The copper sulphide paste must be protected from air by covering it with a little ammonium sulphide; should oxidation nevertheless occur, the sulphide must be placed on a filter and washed with ammonium sulphide and water.

The quantity of oxygen carrier required depends on the amount of aniline and oxidising agent employed, and also on the way in which the development is effected; the more oxygen carrier taken the more rapidly does the colour develop. According to Witz, one part of vanadium chloride is sufficient to convert 200,000 parts of aniline salt into black; in practice, however, a larger proportion is taken: a few milligrams per litre of padding solution. The copper sulphide paste, which is about 30 per cent. strength, is used in the proportion of about 10 grms. per litre (1 per cent.). The action of the vanadium is explained by assuming the formation of a readily decomposible chlorate—that of the copper sulphide by the formation of copper sulphate.

To prepare the padding solution, each of the above-named ingredients is dissolved separately in water (the copper sulphide used being merely stirred up in water), and the resulting solutions mixed in a cold state; the oxygen carrier must not be added until just before use. If copper sulphide be taken, the solution must contain some thickening ingredients, otherwise a sediment would be formed. The material to be dyed is then padded with a prepared solution, dried at the ordinary temperature, and, in order to start the oxidation, is then either passed through a Mather and Platt at a rate of about 60–100 yards a minute, or left for about two days in a slightly humid oxidising chamber at 25–30° C. Nowadays the former method is most in use; the other required some skill to carry out properly.

The pieces placed in the oxidising chamber must be neither too dry nor too damp, since in the former case the colour develops badly and gives a dull brownish black, and, in the other case, development goes on too quickly. The development of the black is

retarded by draught or by too long a sojourn in the cold chamber, the reason for this being a partial volatilisation of the aniline and crystallising of the chlorate so that it can no longer oxidise. The piece turns a progressively darker green in the chamber owing to the formation of emeraldine, and when this shade has reached a certain intensity, further sojourn in the chamber is dangerous, the acid from the aniline salt rotting the fibre. On removing the pieces from the chamber the colour is developed by chroming, after which they are washed and finally soaped hot.

Chroming is effected in various ways, the amount of chromate used ranging from one-fifth to ten grams per litre, in direct relation to the depth of black required. Chroming may be performed in an acid or in an alkaline solution. In the former case the average proportion is one molecule of sulphuric acid to one molecule of potassium bichromate, the material being treated in this solution for about ten minutes at 80° C., or it is treated in a similar fashion (sometimes in the cold) in a solution of chromate rendered alkaline by soda, in which latter event a subsequent soaping is advantageous, though not essential. A good oxidation black can also be produced in the following manner without any oxygen carrier:—The goods are padded in a solution containing 6 per cent. of aniline oil, 6 per cent. of hydrochloric acid, 2 per cent. of copper sulphate, 2 per cent. of potassium chlorate, and 2 per cent. of sal ammoniac (these quantities being reckoned on the weight of cotton to be dyed), then dried, and developed in the oxidising chamber at a temperature not above 27° C., chromed, oiled, dried, and washed. In the introduction of oxidation black in yarn-dyeing, considerable difficulties had to be overcome; in particular, uniform oxidation in the warm chamber only became possible upon the construction of special reels on which the spread-out yarn is caused to rotate. Even now only a few works are fitted up for dyeing yarn in this manner, and for producing the so-called diamond black.

There are two disadvantages attending on oxidation black; in the first place, the hydrochloric acid of the aniline salt always more or less strongly corrodes the cotton fibre, and, where the work is carelessly done, this may extend to a complete rotting of the goods. The second drawback is that the colour turns green after a short time. This change on the part of aniline black apparently results from the formation of emeraldine by reduction, and is the more retarded the deeper the black. An absolutely unchangeable black does not exist. Frequently, in order to improve the colour and mask the change to green, the black is topped with methyl violet. Oxidation black is also produced on any silk goods in just the same way as on cotton, and is generally topped with methylene

blue. Considerable advance in this branch has lately resulted from the introduction of the so-called Prudhomme's black. The *modus operandi* is similar to the later methods, except that potassium ferrocyanide is added to the padding solution. This salt reacts on the aniline chloride, forming aniline ferrocyanide and potassium chloride. It differs from the above-described oxidation black, inasmuch as the fibre is not corroded, the hydrochloric acid being combined with potassium, and that the development of the dye proceeds more gradually: a great advantage in the production of printed goods. The quantity of potassium ferrocyanide depends chiefly on the amount of aniline, the average being about 50 grms. per litre (5 per cent. by weight) of padding solution; no oxygen carrier is required. The goods are first padded, then dried in a current of hot air by passing through a small chamber, and finally developed as in the older processes.

Single-Bath Aniline Black has long been largely used for dyeing loose cotton and yarns, and more recently extended to cotton in warps.

As the name implies, the dye is produced by dyeing the cotton in a single bath; this contains aniline chloride, potassium bichromate, and hydrochloric acid. Some dyers use, instead of hydrochloric, sulphuric acid, or a mixture of the two; and hydrofluoric acid has also been proposed for this purpose (Thiess & Cleff). Others again replace a portion of the chromate by copper sulphate.

The proportions of these reagents vary within wide limits.

As far as the aniline salt is concerned, the quantity depends entirely on the depth of black required, and therefore is limited by consideration of expense. In practice, for this reason, not more than about 11 per cent. of aniline salt or 8 per cent. of aniline oil can be used; even with 8 per cent. of the salt a very good black can be obtained. The average quantity of bichromate is from 1·3 to 1·6 parts per part of aniline salt. Finally, the quantity of acid used differs so considerably in the various recipes that no average figures can be given. Nevertheless, it is irrational to employ more than 12 per cent. of hydrochloric acid; and 8 to 10 per cent. would generally be sufficient.

The dyeing process is performed as follows:—The ingredients are dissolved separately, and mixed in a perfectly cold state just before use. The dye-bath should be as cool as possible, and used in a wooden vessel, the time of exposure being two to two and a half hours. The black will be less likely to rub off if the acid be added in several portions, and not all at once. The cotton is at first coloured green, then blue, and finally black. In order to better utilise the bath, the temperature may be raised to about

60° C. during the last half-hour. The more concentrated the bath the quicker will the colour develop.

The chief point in this method is to secure the development of the aniline as far as possible in and upon the fibre, and as little as may be in the bath, since the black deposited in the bath adheres only loosely to the cotton, and easily rubs off. A good aniline black bath should therefore remain clear as long as possible, although, towards the end of the operation, a deposit is always formed in the bath.

On leaving the bath, the black is of an ugly brown shade, and must be improved by topping with logwood and hot soap. The logwood is fixed by the chrome deposited on the cotton whilst in the dye-bath.

All single-bath aniline blacks have a more or less pronounced tendency to rub off; they are, however, faster to acid than oxidation black, and do not corrode the fibre. The rubbing-off may be considerably diminished by careful washing, preferably in running water after dyeing. Finally, mention may be made of two modifications of this process. In the one, the single-bath black is produced in a warm bath containing less aniline than usual (about 8 grams per litre); the black, however, easily rubs off, and consequently this method is very seldom used. On the other hand, black is still produced on loose cotton by impregnating the material with a concentrated black bath, and then developing the colour by steaming. No advantageous method has yet been devised for recovering the chrome from the spent black baths.

Of the mineral dyes developed on the fibre the following alone are of any practical importance:—Manganese bistre, iron chamois, Berlin blue, chrome yellow, and orange chrome.

Manganese bistre is largely employed in calico-printing, on account of its fastness and the ease with which it is discharged. The goods are first padded with a solution of manganous chloride that has previously, to a slight extent, been converted into acetate by the addition of a little lead acetate. The concentration of the manganese solution is naturally in direct ratio to the depth of brown to be produced. Next, they are passed through boiling caustic soda of about 17° B. strength; then exposed to the air by passing over guide rollers, and, in the case of dark shades, returned to the soda bath. Finally, to ensure complete oxidation, they are treated in a hot bath containing about $1\frac{1}{2}$ part, by weight, of potassium bichromate per 1000, and then washed.

Very good results can also be obtained with manganous chloride alone, or another organic salt of manganese instead of the acetate, though it is advisable, to secure equalisation of the colour, that part

at least of the manganese should be in the form of acetate. The soda solution should be causticised beforehand with lime, since, if it contain carbonate, there will be formed on the material, in addition to manganese hydroxide, manganese carbonate, which is less easily oxidised and may give rise to irregularities in the colour. For light brown, the alkali may be weaker than that mentioned above. The padding with hot lye is effected in a steam-heated apparatus. In some works the final oxidation is performed with sodium hypochlorite, in the cold, instead of with bichromate.

Iron chamois is only sensitive to acids, being in other respects a very fast dye. The iron salt used is the so-called iron nitrate, or iron acetate, prepared from ferrous sulphate and lead acetate by double decomposition, the displacement of the sulphuric acid of the iron salt by the acetic acid being, however, incomplete. The cheaper iron pyrolignite is not so suitable in this case, its tarry impurities muddying the colour.

Even ferrous sulphate does not give good results. The shade of the chamois can be modified by adding aluminium acetate to the iron solution. The method of dyeing is as follows:—The goods are padded with the iron solution, dried, then left twenty-four hours in the warm oxidation chamber, and afterwards treated, for the precipitation of the hydroxide, in a hot (80° C.) bath, containing about 1 per cent. by weight of chalk and 0·3 per cent. of water glass (sodium silicate). Finally, they are washed, dried, and subjected to steam chemicking (*see* Calico-Printing), which gives the colour a more agreeable tone.

This method, however, is confined to the production of discharge effects in calico-printing, the following being that pursued generally in cotton-dyeing:—The goods are passed in succession through an iron bath, a lime bath, and a chemicking bath containing "chloride of lime," these baths being contained in vessels similar to those used for the dunging process. After each bath a good squeezing is given to remove the superfluous liquor, and finally the goods are washed.

Berlin-blue is a bright colour, fast to acids and light, and is still used, though only to a limited extent. The goods are prepared by passing them first through a bath of sodium stannate and then through sulphuric acid, after which they are washed and passed alternately through an iron bath and one of potassium ferrocyanide, until the desired shade is attained.

Chrome yellow and orange chrome are still largely used, both on account of their rich bright tone and because they increase the weight of the goods.

Chrome yellow is particularly fast to light, soap, and acids,

though it is turned reddish by alkalis, and brown (lead sulphide) by sulphuretted hydrogen. The same applies to orange chrome, except that this dye is unaffected by alkalis and is stained yellowish by acids. The behaviour of these two pigments towards acids and alkalis is due to their ready conversion one into the other, chrome yellow being transformed into the basic chromate (orange chrome) by alkalis, whilst the latter is reconverted into the yellow normal chromate by acids. Both pigments are poisonous.

Chrome yellow is produced by depositing lead hydroxide or lead sulphate on the fibre, and then converting the compound into lead chromate by potassium bichromate. This is effected in different ways, especially as regards the fixing of the lead on the fibre. For instance, the goods are impregnated in a solution of lime, then treated in a solution of basic lead acetate, and then returned to the lime bath. Of course, a squeezing must be given after each immersion. The use of a basic salt of lead is explained by the chemical reaction, whereby the lime fixes the acid of the lead salt and deposits the hydroxide of lead on the fibre. Other dyers impregnate with a solution of a lead salt, dry, and then pass through a cold solution of ammonia (1 part to 6 of water) for two minutes. Again, the material is padded with a solution of magnesium sulphate, then dried, padded with a solution of basic lead acetate, and then left at rest for the formation of lead sulphate on the fibre. In any case, a good washing is given after the lead treatment, and the goods are then immersed in a solution of potassium bichromate (5–6 parts per 1000) at 50° C. for half an hour, and finally washed.

For the production of orange chrome, the chrome yellow generated on the fibre is "oranged" by treating the goods for half an hour in a boiling-hot bath containing 1 part, by weight, of lime per mil.

The Albumin Dyes are used only in Calico-Printing, and will therefore be described under that heading.

IV. Dyeing on a Manufacturing Scale.

Textile fibres are dyed on a manufacturing scale in the condition of loose material, rove, yarn, and woven fabrics, the latter being the most usual practice on account of the greater convenience and cheapness, it being possible to handle a larger quantity at a time with a smaller expenditure of dye, owing to the more closely compressed condition of the fibres. Dyeing the loose material is the most expensive form of all, there being a greater consumption

of dye, and more waste during spinning and weaving, owing to the more extensive tearing of the fibres that have become more or less closely matted together in the dyeing. Finally, it must also be borne in mind that some dyes, especially those produced by the aid of tin mordants, increase the difficulties of the milling process. Consequently the dyeing of fibres in the loose state is practised only in the case of better class single-colour fabrics, parti-coloured goods with woven designs, or in the production of yarns and fabrics from mixed fibres. By mixing together a number of loose coloured fibres, and then willowing, carding, and spinning the mixture, a series of shades can be produced that give the finished fabric the appearance of a uniformly coloured product.

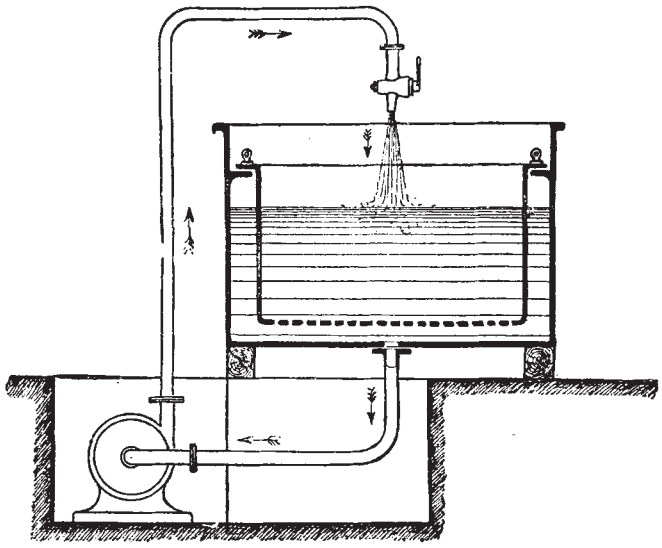

FIG. 28.

In this manner, by an admixture of white fibres with others dyed with dark shades fast to light, a faster light shade can be obtained than is possible by dyeing the whole in the same shade. (*See* Fastness of Dyes to Light.)

In dyeing loose fibres, perfectly soluble dyes and extracts alone are suitable. The vessels employed are generally hemispherical copper vats, the bath being heated by a steam coil under the perforated false bottom. Of late years there is a growing tendency to employ closed vessels, or open vats fitted with a circulation pump (Fig. 28).

Worsted yarn is often dyed in the state of sliver, this condition being more suitable than that of loose wool. The sliver, having

been slightly oiled, must be cleansed before dyeing, for which purpose it is steeped awhile in a very dilute warm solution of soda, then rinsed, and dyed after winding in hank form like yarn. The work must be performed with great care, since the sliver is easily torn and readily felts; the bath must not be boiling hot, nor may the material be worked about too rapidly. The advantage of dyeing in this form rather in the state of yarn, is that any slight inequalities are unimportant, being eradicated during the subsequent spinning process. In order to protect the material, it is now largely the custom to dye the bobbins of sliver or carded fleece in dyeing machines, wherein a circulation of the bath liquor is maintained by suction and pressure, thus forcing the liquor through the material. A typical form of this class of apparatus is the Obermaier revolver shown in Fig. 29.

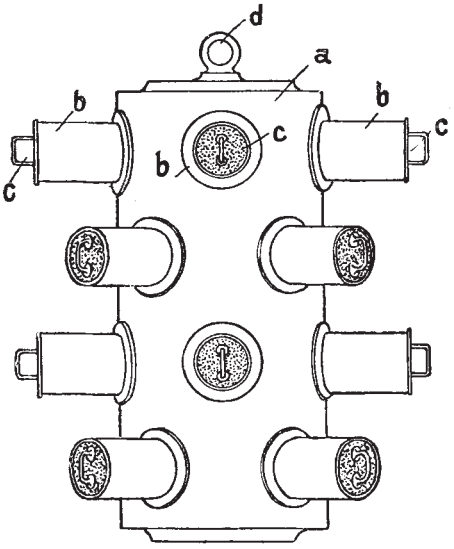

FIG. 29.

This machine consists of the vertical main cylinder *a*, around which are mounted in four horizontal rows a series of small cylinders *b*, each containing a bobbin. At the junction of the bobbin cylinders with the main cylinder are a number of perforations, and similar perforations are made in the lids, *c*, of the bobbin cylinders. In dyeing, the cylinder is placed above the discharge pipe *e*, in the dye-vat *d* (Fig. 30), and the pump is started. The liquor is first forced by the pump into the interior of the main cylinder *a*, thence through the perforations into the bobbin cylinders, where it traverses the material, and thence escapes into the dye-vat. When the tap *g* is closed, the liquor returns to the pump through the raised valve *h*, and the circulation begins anew; when the valve *h* is closed and the tap *g* opened, fresh dye liquor, mordant solution, or water can be run in through the pipe *i*.

The vat is heated by steam-pipes, and is emptied by the tap *h*. This machine can be used for the various successive operations of damping, mordanting, dyeing, and washing, and also for drying

the material by means of hot air. It is advisable to add only one-half the requisite amount of dye at first, then take out the bobbins when the bath is nearly exhausted, and reverse them so that those formerly in the top row are now in the bottom, and so on, the bobbins being also turned end for end in the cylinders.

When these mechanical dye-vats are used, the most soluble dyes should be selected, the materials should be as clean as possible, and the bobbins not too tightly wound.

All fibres are dyed in the condition of yarn, and that, too, more often than the loose state. The general practice is to dye in hanks or in warps, and latterly it has become the custom to also dye in the form of cops, especially in the case of cotton yarn.

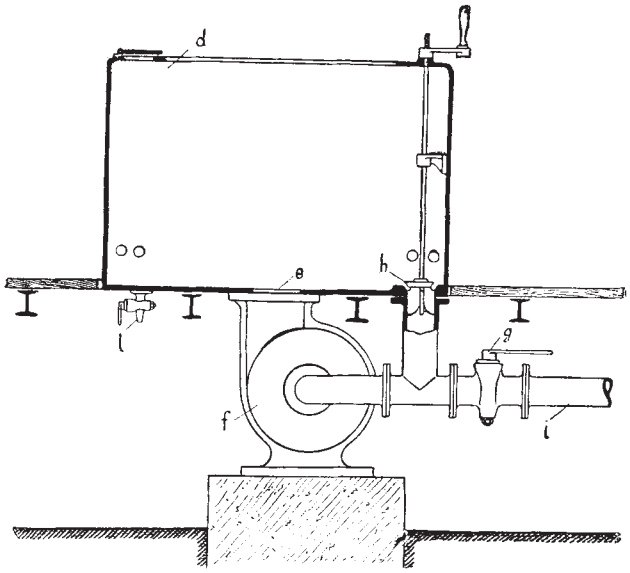

FIG. 30.

Hank yarns are dyed in quadrangular wooden becks (Fig. 31), fitted with a false perforated bottom *b*, underneath which is situated a steam coil *d*, admitting steam to the bath. When, however, the volume of the bath liquor must not be allowed to increase during dyeing—for instance, in dyeing cotton with substantive dyes—a closed steam-pipe is used. The feed steam-pipe *e* must be separated by a wall *c* from the material to be dyed. The method of dyeing is as follows:—The hanks, *g*, are first fastened together by intertwined strings to prevent tangling, and are then hung in rows on smooth rods *f*, arranged crosswise on the edge of the beck. At intervals the hanks must be turned, a row at a time, by passing a rod through the whole row, lifting it out of the liquor, and giving it

about a quarter turn. When it is desired to add more dye to the bath, the depending end of each row of hanks is laid over the adjoining rod. The movement of the bath liquor must not be more than a gentle undulation, in order to prevent tangling or felting in the case of woollen yarn. This defect is also minimised by reducing the period of exposure in the bath.

This method of dyeing entails a good deal of hand labour, on which account numerous hank-dyeing machines have been constructed wherein the yarn carriers are usually caused to rotate by means of toothed wheels, thus turning the yarn mechanically.

For dyeing warps the yarn is conveyed alternately up and down over guide rollers, through several dye-vats in succession.

Cop dyeing has numerous advantages. In the first place, the yarn is delivered from the spinning frame in this condition, which is the most suitable for weaving purposes, whereas, in order to dye

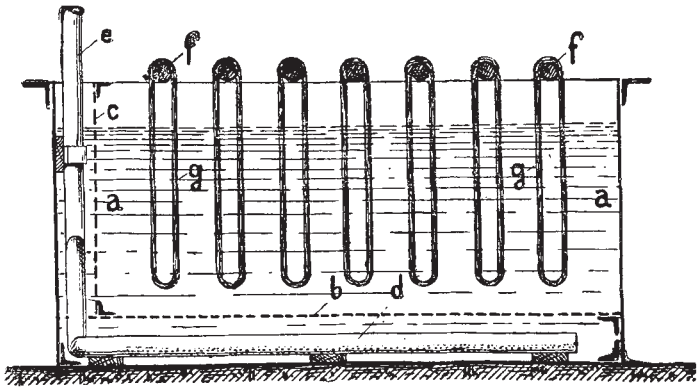

FIG. 31.

the yarn in hanks, it must first be wound into hanks, then dyed, and afterwards rewound into cops, which naturally entails much labour and tends to increase breakage. To prevent all this, a large number of cop-dyeing machines have come into use, though only for cotton, the cop form being unsuitable for dyeing animal fibres owing to the less permeable character of these materials.

Further advantages of these cop-dyeing machines are their higher working capacity, and the possibility of employing softer yarns, which therefore fill up the fabric better.

Readily soluble dyes and simple methods of dyeing alone are suitable for this purpose. For the most part, substantive dyes, the indigo-hyposulphite method, and the Erban and Specht alizarine method, are employed. The difficulties of cop dyeing increase with the number of preparatory operations necessary to the dyeing, and consequently the basic and mordant dyes are little used.

Most of the cop-dyeing machines are based on the principle of forcing the dye liquor through the cops by suction or pressure. The chief thing is to secure equal dyeing, and for this purpose it is therefore necessary that the resistance to be encountered by the liquor should be uniform throughout, in order that it may penetrate equally through all parts of the cops.

Of the numerous types of cop-dyeing machines, only that of Mommer (*see* Fig. 32) need be mentioned here. The principle of the apparatus is as follows:—The cops to be dyed are formed into

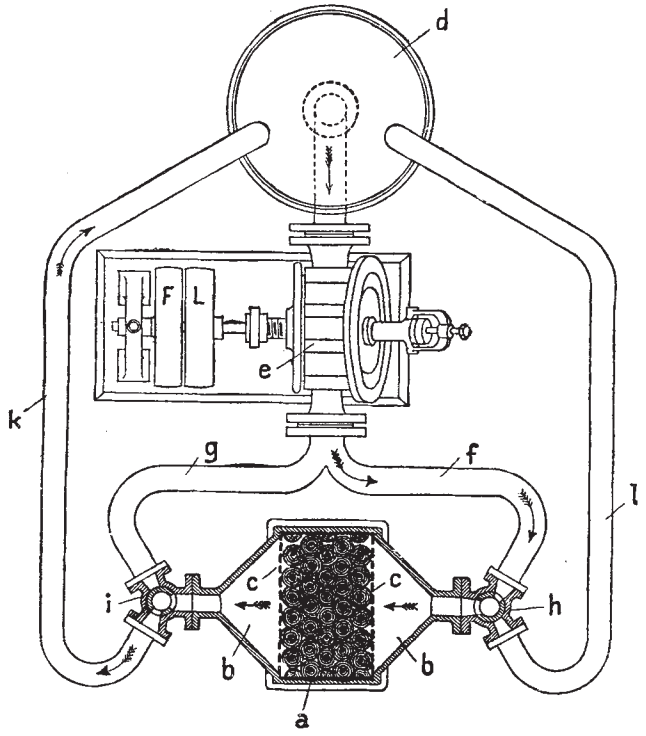

FIG. 32.

a block which presents the same resistance in every direction to the bath liquor. This block, *a*, is formed by placing together a number of frames in which the cops, mounted on heavy spindles, are arranged in parallel rows. Each frame then represents a porous wall of cops, through which the bath liquor can penetrate without difficulty. The block is placed between the two perforated partitions *c* in the closed air-tight chamber *b*, into which the bath liquor is forced by the pump *e* from the vat *d*, through the pipes *f g*, according to the way the taps *h i* are set, so that the liquor traverses the block either from right to left or *vice versâ*.

In the position of the taps as shown in the figure, the liquor passes through the tap *h* into the chamber *b*, traverses the block *b*, and returns through the pipe *k* to the dye-vat *d*. The taps can also be set so that the liquor enters the chamber *b* through the pipe *g* and the tap *i*, and, after traversing the block of cops *c*, escapes through the tap *h* and pipe *l* to the vat *d*.

Piece Dyeing.—The only time when this is a disagreeable operation is when the goods are defective and dirty. Many defects do not reveal themselves until after the goods are dyed, especially

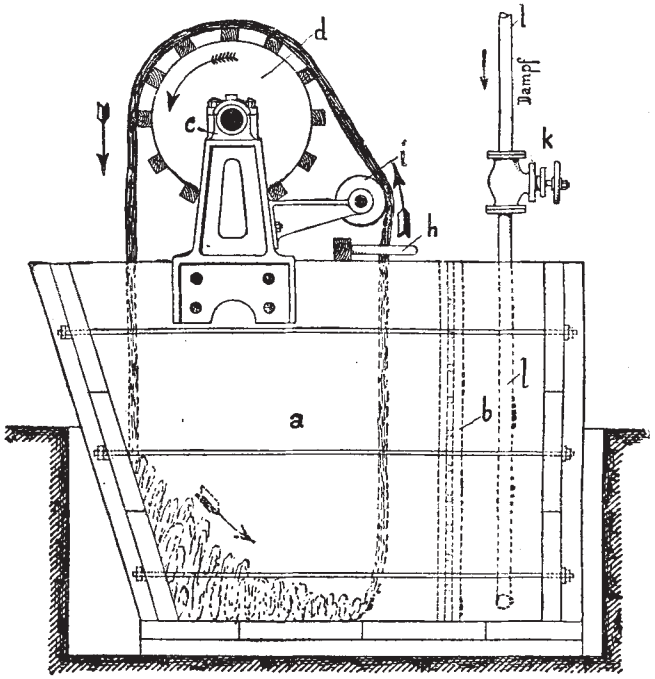

FIG. 33.

when the latter have to pass through a somewhat complex process of manufacture, as is the case with woollen cloth.

In such cases stains appear in the form of cloudy patches or as dark selvedges in full-width dyeing, etc., and this most readily happens when small dye-vats are used, where the central portion of the piece is more compressed than the edges, which latter therefore absorb a larger quantity of dye.

A vat wherein all the operations of piece dyeing, such as damping, mordanting, and dyeing, can be performed in succession is shown in Fig. 33. In this apparatus heat is applied through a steam-pipe *l*, which is separated from the goods by a perforated

partition wall *b*. This smaller compartment also serves for the introduction of the added solution of dye.

The pieces are sewn, end to end, in the form of an endless band, and generally reeled like a hank. If to be dyed full width, the piece is kept spread out by the aid of a stick in the hand of an attendant whilst slowly passing through the dye. More frequently several sets of pieces are wound side by side on the same reel, and are kept separated by lattice partitions during their passage through the dye-vat, in order to prevent them from getting mixed on the reel. Cotton goods are dyed in the same way, mostly in hank form.

A machine largely used for dyeing piece cottons is the jigger, Fig. 34. It consists of a simple wooden vat *a*, on to which are screwed the cast-iron uprights *b c*, supporting the wooden rollers *d e*. The goods, which are wound on the roller *e*, are drawn through the dye-bath in the direction shown by the arrow, when *d* is set in motion, and are then wound up on the roller *f*, which is mounted in a slotted bearing. The roller *e* is fitted with a loaded brake in order to keep the goods at the proper tension. If the goods have to be passed through the bath for several hours in succession, they are wound on *d* at first instead of on *f*. On motion being imparted to the roller *e* and the brake applied to *d*, the goods traverse the bath in the opposite direction, and are wound up on *e*. The jigger is the best machine for dyeing piece cottons with substantive dyes or basic dyes.

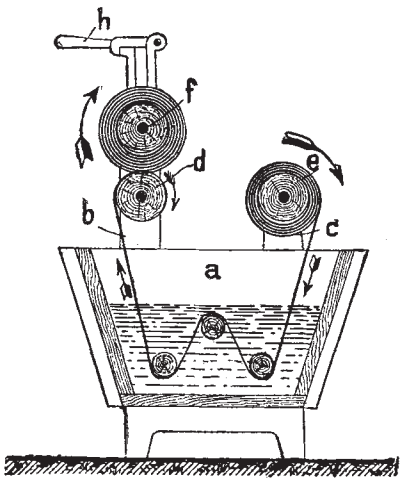

FIG. 34.

Before setting the dye-bath the water must be corrected or purified by boiling with soap or bran. The whole or a portion of the dye is then added. The usual method of dissolving the dye is to mix it into paste with a little hot or cold water and then suffuse it with a larger quantity of hot water, pass it through a linen filter, and run it into the vat; the undissolved residue is brought into solution by a further addition of water. As a rule, it is not advisable to place the solid dye-stuff in the vat. Distilled or condensed water should be used for dissolving dyes; in the case of basic dyes, a little acid facilitates solution, whilst soda is often

useful as an adjunct in dissolving acid dyes. Dyes in paste form must be carefully stirred up with water.

After dyeing, the goods are generally rinsed, to remove adherent impurities and dissolved dye. Loose materials are rinsed in rinsing machines; yarns in the hank are usually hand-washed in the dye-vat, the dye liquor being drawn off and replaced by fresh water. There are also yarn-washing machines, wherein the yarns are suspended from revolving rollers. Washing in running water is the most efficacious. Piece goods are washed on the reel; in the case of fugitive dyes the pieces are passed full width through becks fitted with rollers. Owing to the multifarious character of the operation, it is impossible to go further into details.

The dyed goods are drained in the hydro-extractor. Drying is effected, in the case of loose material, in special forms of apparatus, frequently by the aid of hot air in carbonising machines. Yarns and piece goods are dried by hanging in warm chambers; piece goods more frequently in revolving cylinders, stretching frames, and calendering machines, similar to those used in the finishing process.

The Selection of Dye-Stuffs for Dyeing.

The kind of dye-stuffs to use for producing a particular colour depends both on the nature of the fibre and on the form in which it is to be dyed, and finally also on the requirements exacted of the colour itself.

Cheap dyes will be chosen for cheap goods, and dyes fast to light for goods that will have to be exposed to the light a good deal. In dyeing loose wool the prime consideration is fastness to milling on the part of the dye, whilst in dyeing yarn and piece goods the equalising properties must chiefly be borne in mind. In short, the dyer must not only be in a position to produce a given shade of colour in dyeing, but he must also have an accurate knowledge of the behaviour of the various dye-stuffs and their combinations towards the influence of light and the various other agencies (*see* Tests for Fastness) that may have to be encountered.

Silk-Dyeing.

Silk is dyed in the hank form almost exclusively, very rarely loose. Hand in hand with this operation goes that of loading, which is almost the more important of the two.

It is only in exceptional instances that special requirements in respect of fastness are exacted of silk-dyeings. The dyes most suitable for the purposes of the silk-dyer are those enabling him to

produce all imaginable shades of colour in a rapid and easy manner, with perfect equalisation, the chief qualities being good capacity for equalisation and combination. In comparison with wool and cotton, the number of dyes employed is remarkably small, and these mostly belong to the group of acid dyes, the following being most in use :—

Greens : acid green, malachite green.

Yellows : quinoline yellow, citronine, azoflavine S ; naphthol yellow and picric acid are often employed for shading in the brightening bath.

Orange : orange II, 2R, etc.

Brown : acid brown.

Reds : Several ponceaus, roccelline, azocarmine, rhodamine, phloxine, primrose, Magdala-red.

Violets : acid violet, methyl violet, violamine.

Blues : alkali blue, marine blue, methyl blue, induline.

Of these the most suitable for combination are citronine, orange II, roccelline, rhodamine, phloxine, methyl violet, methyl blue, and marine blue.

Colours fast to water are obtained from citronine, roccelline, and marine blue, by solidification after dyeing.

For colours to stand soap, the dyes most frequently used are a few alizarine reds (powder), alizarine orange, cœruleine, and galleine.

Black, the most important dye for silk, is obtained with log-wood only.

Wool-Dyeing.

Wool is dyed in the loose state, as sliver, yarn, and in the piece after weaving ; sometimes also in two stages of manufacture, *e.g.* by vatting in the loose state and topping in the piece.

Of all fibres wool is the hardest to damp, and is therefore best dyed at boiling-heat. Consequently, dyeing in the vat, an operation performed at medium temperatures, affords a very sharp test as to the capacity of any sample of wool for absorbing dyes.

The chief dyeings for wool are blue, red, and black. A very large number of dyes, singly and in combination, are used, the most popular and suitable of which will now be described, without any claim being made to absolute completeness.

Green.—A number of bright shades, bearing the name " billiard green," are produced on woollen cloth. Formerly these were obtained from fustic, indigocarmine, and alum (in a single bath), but now-adays acid green is used exclusively, either alone or shaded with some yellow dye, such as naphthol yellow, quinoline yellow, fast yellow, or tartrazine, or by combinations of patent blue or indigocarmine

with one of the above yellow dyes. A particularly pure green is furnished by patent blue N and quinoline yellow.

A brilliant green, fast to milling, is produced on yarn, by the use of milling yellow O (C.) and patent blue A (M.L.Br.); on loose wool with anthracene blue WG extra (B.A.S.F.) and alizarine yellow GGW (M.L.Br.). Unfortunately, however, the last-named excellent dye will not entirely resist the influence of carbonising.

A series of dull olive green tones are produced by combinations of red, blue, and yellow, *e.g.* with chromotrope, azo acid yellow, and patent blue; or with ponceaus, a yellow, and acid green; or, finally, with fustic and logwood.

A very dark, almost black, fast green is obtained by dyeing the loose wool with fustic and alum, and then vatting.

Yellow.—Bright shades of yellow are obtained with quinoline yellow, naphthol yellow, tartrazine, fast yellow, etc.; all these dyeings, however, are incapable of withstanding washing, and, except the two last named, are fugitive to light. They are employed for equalising (trimmings for uniforms) and for many yarns. Faster dyeings are obtained by means of milling yellow O (C.) and with quercitron, or flavine, on zinc-alumina mordants. The two latter dyes reduce the milling fastness of the wool. A beautiful yellow that will completely withstand carbonising can be produced by dyeing with alizarine yellow GGW (M.L.Br.) and potassium bichromate in a single bath.

Anthracene yellow C (C.) gives a very clear yellow, of greenish tinge, furnished by dyeing in an acid bath and then treating with chromium fluoride, the dye being less fast to milling when applied to previously mordanted wool.

Dull greenish yellow colours are produced on loose wool by galloflavine, or cœruleine and fustic, on chrome mordant; on yarns and piece goods by an orange and an acid green.

Orange is produced with one of the orange acid dyes, or with a ponceau and one of the yellow dyes already mentioned. For fast dyeings, cochineal and flavine are used on tin mordant; if duller shades are desired, flavine is replaced by quercitron, and a tin-alumina mordant is used.

Reds.—The chief shades of this important colour are scarlet and madder red (a duller brownish red). For fast scarlets use is made of cochineal on tin mordant; for fugitive kinds, the various ponceaus. Madder shades are also produced with ponceaus; faster kinds, with cloth red or alizarine.

It should be mentioned that considerable divergence exists in the fastness of the various ponceaus, a circumstance still insufficiently known and appreciated in practice. Some of these dyes are

just as fast to light as cochineal; but without exception their fastness to milling is not good, since all of them bleed into the white during that process, though even in this particular differences exist. All of them have a greater capacity for penetrating the fibre than cochineal—the palatine scarlets in particular.

The fastest to light of all the ponceaus are the palatine scarlets (B.A.S.F.), the Victoria scarlets (M.L.Br.), brilliant ponceaus, 4RS, 3R, 4R (C.), a few marks of brilliant croceine (C.), croceine scarlet R (By.), croceine 3B, RX (By.), etc. The palatine scarlets are identical with dyes sold under other names; palatine scarlet A, for example, being the same as Bayer's cochineal scarlet PS and Cassella's brilliant cochineal. Those furnishing the more bluish shades are ponceau B extra (M.L.Br.), scarlet B (By.), new red 5R (By.), a few B marks of brilliant croceine (C.), etc.; ponceau B extra, and scarlet B being the best as regards milling fastness. These two can be used for goods that are to be milled, but must then be dyed by the aid of tin chloride and potassium bitartrate; and the milling must be conducted with care. Colours that will stand sulphur are furnished by, *e.g.*, ponceaus 2R, 3R, (M.L.Br.) and the cheap double ponceau 4R (By.).

The best means of producing, on loose wool or yarns, colours that will not bleed into the white when milled, is by the employment of a red substantive dye. The most suitable for this purpose is the excellent dye, delta purpurine (dyed with common salt and potash); also brilliant Congo R, fast diamine red, anthracene red, Hessian purple N, etc. Many of the substantive dyes, like delta purpurine, brilliant Congo R, fast diamine red, etc. are also fast to sulphur, an essential condition for goods that are to be sulphur-bleached.

The fastest red on wool is produced by means of alizarine (powder) on a mordant of alumina, chrome, and tin. For a madder red these mordants are used in the following proportions:—

Alum	12 per cent.	
Tin salt	1½ „	
Potassium bichromate .	1 „	
Potassium bitartrate . .	4 „	
Oxalic acid . . .	4 „	(with water of about 20° of hardness).

A colour of the same appearance can, it is true, be obtained with alumina and alizarine alone, but is not thoroughly fast to milling.

Of course this by no means exhausts the list of red dyes applied in practice to wool, other shades (crimsons) resembling fuchsine, of a fugitive character, being produced on piece goods with fuchsine,

fast ones with fast acid violet A2R (M.L.Br.), or cheaper ones with azo acid fuchsine and similar dyes.

Rose Red is applied only to woollen yarns and piece goods, the dyes used being cochineal, with tin mordant, rhodamine—and also other eosines, when the shade requires,—chromotrope, etc. Diamine rose (C.) is also suitable for this purpose.

Bordeaux is produced, as a dark shade, fast to milling, on loose wool and on yarn by means of alizarine and chrome mordant. This colour bleeds slightly, but can be improved in this respect by adding copper sulphate to the mordanting bath. In piece dyeing this colour is mostly obtained with aniline dyes, various fast reds—among which special mention is deserved by the extremely powerful fast red O (M.L.Br.),—also with Victoria rubine and others, the shade being darkened, if necessary, with a blue dye, like cyanine or patent blue, or yellowed with an orange or an acid yellow. These red dyes are handsome and sufficiently fast to light, but do not equalise well. For this reason many dyers prefer to dye with a ponceau or chromotrope, and darken with a blue.

A bright Bordeaux, very fast to light, can be obtained by the aid of fast acid violet A2R (M.L.Br.), chromotrope 2R, orange C, and a blue.

A Bordeaux that is faster than can be obtained from aniline dyes, and of a shade not obtainable with alizarine dyes, is furnished by mordanting with alum, tin salt, and potassium bitartrate, dyeing with cochineal and madder, and darkening with archil according to requirements.

Blue.—This is perhaps the most important of wool colours, and is produced in a variety of ways.

For medium and dark blues, indigo is the first dye to be considered, because it furnishes the fastest dyeings, or the so-called "fast blues." The wool is dyed in the vat both as loose wool, yarn, and in the piece, though, owing to the difficulty of obtaining proper equalisation by this last means, it is a general custom to blue wool in its loose state. "Semi-fast blue" is produced in two ways, the vat-blued pieces being either boiled with santal, or first mordanted with alum, copper sulphate, and bitartrate, and then dyed with logwood, as already described. The blue obtained with the aid of sandars is much faster than that topped with logwood. Vat blue is also frequently topped with methyl violet or an aniline blue, to improve its brightness, or bottomed with azofuchsine (By.) to save indigo.

Many medium and dark blues, for the most part on yarns and piece goods, are produced with blue alizarine dyes and chrome mordants; of these, special mention may be made of anthracene blue WG extra (B.A.S.F.), on account of its beauty and cheapness.

"Wood blue," which is bright and fast to washing, though fugitive to light, is still largely produced on piece goods.

Similar dyeings, of satisfactory fastness, are also extensively obtained with sulphone cyanine (By.)—which is characterised by great fastness in wear and its resemblance to indigo blue—and naphthol blue (C.). So much, however, cannot be said of the various fast (induline) blues also in use, since most of them equalise badly, and, though fast to acid, are fugitive in the light. The recently introduced naphthazine blue (M.L.Br. and Dahl) is not very fast to light, but has the great advantage of not being affected by impurities in the goods.

A number of blue dyeings, known under the names "navy blue," "Tegethoff blue," etc., are most easily produced with acid violet and acid green, or faster with logwood, acid violet, iron and copper mordants, and oxalic acid, in a single bath. Indulines are also used in combination with logwood, by mordanting as for wood blue, and then dyeing.

The so-called "potash blue," formerly produced with logwood and ferrocyanide, is now most frequently dyed with patent blue, acid violet, and a small quantity of orange.

Bright light blue dyeings are produced—generally on yarns—with alkali blue, or the somewhat faster (to milling) alkali violet, whilst perfectly milling-fast blue is obtained by combining alkali violet and milling yellow O (C.). Lighter tones are preferably produced with Victoria blue, or, if required somewhat greener, with patent blue, etc.

A number of dull pale blue to grey shades, known as "pearl," etc., are dyed with patent blue and an easily equalising acid violet, and, if necessary, shaded with yellow; in the case of alizarine blue, anthracene brown, cœruleine, etc., are used for shading, the same dyes being used for shading after alizarine cyanines and chromium fluoride in a single bath; also by blueing in the hyposulphide vat, and topping with alizarine cyanines and chromium fluoride, with archil and indigo-carmine, etc.

In these dyeings the imperfect fastness to light of alizarine blue is only apparent in the lighter shades; this dye can, however, be replaced with advantage by patent blue, or the fairly light- and milling-fast fast acid blue R (M.L.Br.), notwithstanding its low equalising properties. To ensure fastness, however, the aid of the hyposulphite vat is essential.

On loose wool a fast grey, of a shade unobtainable with alizarine dyes, is produced by blueing in the vat, topping with fustic and sumach, and darkening with iron.

Violet is met with either as very vivid violet or as purple. Bright, but fugitive, dyeings of this class are produced with methyl violet or acid violet; darker, duller, and faster shades with galleine, and the fastest of all with alizarine and alizarine blue on chrome mordant.

So-called purples are most frequently produced, on piece goods, by topping vat blue with chromotrope or a ponceau, or with cochineal and alumina-tin mordant. These dyeings are also frequently produced on yarns and piece goods with an acid violet or a good equalising red and blue dye.

Drab.—This colour is obtained solely by the combination of red, blue, and yellow, a distinction being drawn between aniline drab, alizarine drab, and dye-wood drab, according to the class of dye used.

Though deficient in fastness, the aniline drabs exhibit special advantages for piece dyeing, and play a great part in that branch. Their chief superiority consists in the ease with which the desired shade can be obtained, and in the possibility of dyeing in a perfectly uniform manner goods that are impure or contain different wools, more satisfactorily than with alizarine or wood dyes. Only such dyes as equalise well are used for this purpose, most frequently the following:—Chromotrope, 2R (M.L.Br.), azofuchsine (By.), azocarmine (B.A.S.F.), archil substitute N (C.), fast acid violet 10B (By), azo yellow and allied yellows, various acid orange marks, fast yellow, tartrazine, quinoline yellow, various patent blues and cyanines, cyanol (C.), fast green, bluish (By.), wool green S (B.A.S.F.), etc.

The following general remarks apply to these dyes:—The fastest to light are the reds, the yellows coming next, whilst the blues are far inferior in this respect. Chief among the reds, in point of fastness to light, are chromotrope and azofuchsine, the best in equalising power being azocarmine and (the fugitive) fast acid violet 10B. Of the yellows, the fastest to light are fast yellow and tartrazine; of the blues, cyanine, a few patent blue marks (A.V.N.), and cyanol. Tartrazine is the poorest equaliser, but is very productive and gives handsome colours, fast to light and water. Azofuchsine does not equalise well except at boiling-heat.

Aniline drabs are liable to change their colour, more especially when the yellowing has been effected with an orange dye. The combination of chromotrope, cyanine or cyanol, and a yellow like azo yellow, least exhibits this tendency, and is also advantageous in other respects. Another peculiarity exhibited by light drabs is the phenomenon of "insolation," whereby the yellow entirely disappears on exposure to strong light, and thus alters the shade completely. In the dark the original colour reappears. This

peculiarity is probably due to the fact that the goods become drier in the light, and is especially noticeable in the case of fast yellow and metaniline yellow.

The dye-woods (logwood, fustic, and redwood) are mainly employed for pale drabs dyed in the wool by the single-bath darkening method. In this case, aniline drab is too fugitive to be used, and alizarine drab is less easy to dye. For dark shades, wood drab is previously mordanted with chrome; but this is seldom practised, since the dye makes the fibre hard. Finally, alizarine drab is most frequently employed for fast drab in piece dyeing, and for dark drab shades dyed in the wool. It is produced by mordanting with chrome and dyeing with anthracene brown, shaded afterwards with other alizarine dyes, galloflavine, fustic, etc.

For fast drabs, easy of production, more attention should be bestowed on chromogene (M.L.Br.); it is dyed in an acid bath, and afterwards treated with potassium bichromate. A drab that can be equally recommended, especially for yarns, can be produced, more simply and faster than with the above dyes, by the sulphone dyes (By.).

Finally, brilliant alizarine cyanine 3G can be recommended for drabs and mode colours. It is applied in an acid bath, and gives much faster dyeings than those with blue dyes.

Brown.—The chief part in this class of colours is played by anthracene brown, though in piece dyeing the production of wood brown, finished by darkening, is still largely practised. For the reasons named in connection with drab dyeings, the last-named dye is unsuitable for loose wool; it is, however, still used, though santal must be replaced by alizarine orange (eventually by alizarine red or cloth red). The same aniline dyes that are used for drab also find employment for brown-dyeing piece goods.

Black.—For the production of this important colour, the following shades and dyes come under consideration:—Iron black, chrome black, single-bath logwood black, diamond black (By.), alizarine black (B.A.S.F.), also the acid blacks, naphthol black or brilliant black (C. and B.A.S.F.), naphthylamine black (C.), naphthyl blue-black (C.), anthracene acid black (C.), Victoria black (By.), wool black (Act. and By.), Biebrich patent black (Kalle), sulphone black (By.), chromotrope black (M.L.Br.), azo acid black (M.L.Br.), etc., alizarine cyanine black G, and alizarine blue-black B (By.) are too dear for black, though suitable for green.

Logwood black, that at one time was almost the only black, has now been largely displaced by the artificial dye-stuffs. The black acid dyes, most of them fast to light, such as naphthol black, naphthylamine black, etc., owing to their simplicity of application,

and to the fact that the dyeing is not followed by careful washing, are largely used, especially for dyeing pieces containing fancy cotton threads that are intended to remain white after dyeing. However, with the exception of anthracene acid black, they are not sufficiently fast to milling, and many of them are used solely on account of their low price, cost being the deciding factor. The acid dyeings with anthracene acid black will stand careful milling without bleeding into the white. The blacks fixed with chrome mordants—alizarine black and diamond black—are fast to milling; moreover the first of them is the fastest towards acids of all the black dyes, though, on the other hand, its fastness to light is incomplete. Conversely, diamond black is particularly fast to light.

The logwood blacks differ considerably as regards their fastness to light, according to the method of production employed; chrome black is fast to acids, but not to light, though in this respect it is improved by the addition of copper sulphate; iron black is specially fast to light, but very sensitive to acids. As a rule, the logwood blacks have a great tendency to rub off. Iron black still remains the best black for wool, on account of its excellent equalising powers, covering power, aud fastness to light. In some instances it is impossible to dye dirty and nopped fabrics black except with logwood; and few of the above-mentioned dyes can equal it in fulness and beauty of colour. In the case of very dense shades, however, logwood gives a rather brownish black, and better results are furnished by naphthylamine black 4B.

For loose wool and yarns, use is generally made of alizarine black, diamond black, and chrome black, since iron black makes the fibre hard. On the other hand, acid dyeing blacks and iron black are chiefly used in piece dyeing.

Cotton-Dyeing.

Cotton is dyed in the loose condition, as yarn, warps, cops, and in the piece. In the case of this fibre it is a still more difficult task than with wool to give all the various dye-stuffs and combinations used, chiefly on account of the very large number of direct dyes now so extensively employed for cotton. Consequently the subject can only be treated in an indicative manner.

In the first place, it should be mentioned that nearly every dyeing on cotton can be performed in three ways—with tannin dyes, with direct dyes, and with mordant dyes.

Green.—This class of colours is produced with a basic green dye (brilliant green, malachite green, etc.), either alone or shaded with chrysoidine—or handsomer and faster with auramine,—or

with some blue, such as methylene blue, Nile blue, etc., and auramine. Of the direct dyes, the following can be combined to form bright but fugitive greens:—Thiazol yellow (By.), or thioflavine (C.), with diamine pure blue (C.), or benzo pure blue (By.). For medium shades diamine green (C.) has made its way into favour; the dyeings must, however, be brightened by topping with a basic green dye, the colours produced by diamine green alone being too dull. A fast bright green is furnished by quercitron and a basic green dye, mainly on piece goods. Different fast olive green shades can be obtained, chiefly on loose cotton, by the use of logwood and fustic or quercitron, with or without catechu and basic dyes.

Yellow.—Pure fast yellows are produced on cotton with quercitron and alumina mordants, on piece goods, but chiefly with chrome yellow in the case of yarns. Less fast, though still fairly so, are the colours produced with various yellow direct dyes, such as chrysamine (which is cheap, but not fast towards alkalis), chloramine yellow (By.), fast diamine yellow (C.), chrysophenine (By. Act.), diamine golden yellow (C.), Mikado yellow (Leonhardt), etc. Fugitive greenish yellow tones are furnished by thioflavine, thiazol yellow, etc.; faster shades with auramine. Brownish yellow shades, known as chamois, nankeen, etc., were formerly produced with fugitive basic dyes—chrysoidine, phosphine—but nowadays better with chrysamine and similar direct dyes. Iron chamois is the only one that is really fast.

Orange.—A perfectly fast orange is produced, chiefly on yarns, with orange chrome, and with alizarine orange on piece goods. Of the substantive orange dyes, Mikado orange and toluylene orange may be mentioned on account of their fastness.

Red.—The fastest red on cotton is the Turkey-red produced by the old process, the so-called "old red." The new red, chiefly produced on yarns and pieces, is also very fast, though not equal to the old red. In addition to the competitors of Turkey-red already given, the following may also be mentioned—fast diamine red (which is fast enough for many purposes), primuline red, which is fast to washing and is largely used in dyeing yarns, and the red produced with fuchsine or safranine, with or without auramine.

Rose-Red.—The handsomest of these colours on cotton is that furnished by rhodamine and a fatty acid salt of alumina; the fastest by alizarine. When alizarine cannot be used, it may be replaced by erica (Act.), brilliant geranine (By.), diamine rose (C.), etc., all of which yield colours that will stand washing.

Bordeaux.—A fast Bordeaux is produced by combining alizarine

with methyl violet or rubine, or with alizarine, logwood, quercitron, and alumina-iron mordant, on piece goods.

Colours of inferior fastness can be obtained both with direct dyes, *e.g.* primuline red and diamine black, as well as with tannin dyes, the best way, in the latter case, being by the combination of safranine with methylene blue and auramine.

Blue.—Vat blue is the fastest and most esteemed blue for cotton, though the other dye-stuffs already mentioned as rivals of indigo (*q.v.*) are largely used. Fast, handsome, and pure blues can be produced with basic dyes, such as methylene blue. Finally, mention may also be made of Berlin-blue, which is a fast dye and one still used.

Violet.—A perfectly fast colour is obtainable with alizarine on iron mordant, or with gallocyanine on chrome mordant. By itself the alizarine iron violet is too dull, and must be enlivened by topping with methyl violet. These colours are almost entirely confined to calico-printing and to dyeing in the piece. A brighter, and fairly fast imitation of alizarine violet is obtained by combining safranine with methylene blue, methylene violet, and similar dyes. Very bright and handsome, though fugitive, violet shades are furnished by the various methyl violet marks. Of the direct violet dyes the most important are benzo violet R (By.) and diamine violet (C.).

Brown.—The most usual method of producing fast browns and drabs, chiefly on loose cottons and yarns, is with catechu, either alone or in conjunction with other dyes. These are often topped with Bismarck brown, to make them brighter. Fast browns on piece goods are also produced with manganese bistre and by combinations of alizarine, quercitron, and logwood. Finally, also, various direct brown dyes, chiefly diamine brown M, diamine bronze, toluylene brown, new toluylene brown, benzo chrome brown, and benzo brown, are employed, either alone or mixed, and either after-chromed or not.

Grey is still most frequently produced by alternate immersion of the cotton in logwood and iron baths. These dyeings make the fibre hard, and have therefore been largely superseded by various marks of diamine black and similar direct dyes.

Black.—This important colour is now mostly produced with aniline black, and to a lesser degree with logwood. Various direct dyes are also used in the black dyeing of loose cotton and yarns, *e.g.* the different marks of diamine black (C.), direct deep black (By.), direct blue-black (By.), and Columbia black. Less esteemed are the blacks diazotised and developed on the fibre; various marks of diamine black (C.), diaminogene (C.), diazo black (By.), diazo

brilliant black (By.), Zambesi black (Act.). Of greater importance are the after-chromed blacks, various marks of diamond deep black (C.), benzo chrome black (By.), and Columbia chrome black (Act.) (a mixed black), which are fast to rubbing and crabbing (*see* Finishing), and are used to replace aniline black in dyeing half-woollen goods, the cotton yarn being dyed black, spun with white wool, and the wool topped in an acid bath after crabbing.

Vidal black and fast black (B.A.S.F.) are also used for cotton.

In point of fastness, beauty, and fulness of colour, aniline black is the best black for cotton. Logwood black is really only fast when produced by the aid of copper. Most of the substantive black dyes will stand washing, but their fastness to light leaves a good deal to be desired, and they have not the same beautiful full appearance as the aniline blacks.

Ramie, Linen, and Hemp are dyed in the same way as cotton; Jute is dyed with basic and acid dyes in a weak acid bath, either containing alum (2–5 per cent.), or oxalic acid (1–2 per cent.). The material is entered at 40° C., heated to boiling, and boiled for a half to three-quarters of an hour.

Dyeing Mixed Fabrics.

The term "mixed fabrics" implies fabrics composed of two or more different classes of fibres. Formerly these fabrics were dyed, in part or altogether, in the form of yarn, but nowadays they are dyed in the piece, by one of two methods, either to one colour, the different fibres being caused to absorb dyes of the same shade, or else "shot" effects are produced by dyeing the different fibres to widely different colours, the result being the more handsome in proportion as the two colours are complementary one of the other.

The suitability of different dye-stuffs for dyeing mixed fabrics can be readily ascertained by dyeing small samples. In this connection it must be borne in mind that not only the nature of the different fibres present, but also their relative proportions in the mixture, is of importance.

Dyeing Half-Woollen Goods (Wool and Cotton).—It is even now the practice occasionally to dye the cotton, in the yarn, with acid-resisting dyes, then weave it along with white woollen yarn, and dye the wool with acid dyes in the piece. For the most part, however, these goods are piece dyed, there being two methods of effecting this object; the older plan is to dye the wool in the fabric with acid dyes, which, of course, leave the cotton untouched, the latter being afterwards dyed on the jigger by the aid of tannin,

fixed with tartar emetic (and iron, if necessary) and followed by treating with a basic dye. In order to preserve the wool as much as possible from alteration, the latter process is carried out in the cold. The final bath may also be lukewarm, but as the wool always absorbs a little of the dye, the shade produced in the first dyeing should be rather lighter than that really required. In the case of two-colour effects the last dye bath must be cold.

This method therefore entails the use of four baths; and the production of blacks is even more complicated, the cotton having first to be mordanted with iron by treating it with sumach, fixing with iron, and treating with chalk; the wool mordanted next by heating in a bath of potassium bichromate, free from acid (to prevent the iron being extracted from the cotton); and, finally, the whole is dyed with logwood.

In the second method the half-woollen material is dyed with direct dyes in a bath containing 2 per cent., by weight, of Glauber salt. This process has the great advantage of simplicity, inasmuch as a black can be dyed in a single bath, *e.g.* with half-wool black (C.), the only difficulty being in dyeing to pattern.

The behaviour of the direct dyes towards wool and cotton is somewhat divergent, some of them enabling the two fibres to be dyed to an equal depth, whilst others dye the cotton only, and are therefore suitable for use in producing two-colour effects. As a rule, the following conditions obtain: in a boiling-hot bath the wool will take up the more dye and come out deeper in colour than the cotton, the converse being the case when a low temperature is used. The addition of a small quantity of an alkali salt, like soda, reduces the absorption of the dye by wool; and, conversely, the wool is dyed more strongly than the cotton when an acid bath is employed.

The *modus operandi* is thus practically revealed. The goods are entered in the bath, which is then raised to boiling in about a half to three-quarters of an hour, and is kept on the boil until the colour of the wool is only a little lighter than it should be when finished. Steam is then turned off and dyeing continued in the cooling bath until the colour of the cotton appears deep enough. The after-darkening of the wool, which is nearly always necessary, is effected with acid dyes, whilst for the cotton, direct dyes are used, these drawing better on this fibre than on wool; or the dye may be caused to draw more to the cotton or the wool, as is found necessary, by making the bath liquor alkaline or acid.

Dyeing Half-Silk Goods (Silk and Cotton). — There are two chief methods to be considered in dyeing half-silks—(1) the silk is dyed first, with an acid dye, to a shade rather

lighter than actually required, next the cotton is treated with tannin, passed through a bath of tartar emetic, and cold-dyed as quickly as possible with basic dye in a fairly concentrated bath; (2) in this case a first dyeing is given with a direct dye, after which the silk, which is generally too light, is darkened by entering in a bath of basic or acid dye.

This second method has now attained a high degree of practical importance, and will therefore be described in detail.

A study of the behaviour of the various direct dyes towards silk reveals considerable divergences, which, nevertheless, can be classified according to certain laws. In the first place, some of these dyes have the property of dyeing silk and cotton in different tones, and these dyes are the least suitable of any for the purpose now in view. Their affinity towards the two fibres in question depends, in the first place, on their nature, and, secondly, on the constitution of the dye-bath—a greater affinity for cotton being exhibited in a neutral bath containing common salt, or in a weak alkaline bath, whereas in a weak acid bath the dye draws better on the silk. Some of the direct dyes—the reds, for instance—dye cotton and silk almost equally in an alkaline bath, which is charged with 5 per cent. of sodium phosphate, 5 per cent. of soap, and the necessary quantity of dye, the goods being entered lukewarm, then slowly raised to a temperature a little below boiling—not quite on the boil, or the silk would suffer—and, after turning off the steam, continuing to treat in the cooling bath for another half-hour or so.

Many other direct dyes, especially such as dye cotton best in presence of common salt, can be advantageously employed to dye half-silks with common salt and acetic acid, provided the foregoing precautions be borne in mind.

The silk, which is generally rather too light in colour, can be brought up to the proper shade by entering the goods in a fresh bath containing basic dyes and a little acetic acid, at 30–40° C., or with acid dyes at a somewhat higher temperature, and with more acetic acid.

For "shot" effects the goods are dyed either by the first-named method, or else first with a dye that attaches itself to the cotton alone, leaving the silk undyed, the latter being afterwards dyed in a fresh bath containing acid dyes.

Dyeing Gloria (Wool and Silk) Fabrics.—This method of piece dyeing is of recent date, and is one of the most difficult tasks the dyer is called on to perform, since it entails an accurate knowledge of the behaviour of the dyes towards wool and silk.

Here also, as in the case of half-silks, it may happen that the dye produces a different shade on the wool to that imparted to the silk, *e.g.* azo acid fuchsine, fast acid red A (M.L.Br.), etc., which are therefore unsuitable for the purpose in view.

The acid dyes are those most in use for this purpose, and these, as a rule, dye the wool more strongly than the silk when applied at boiling-heat, the converse being the case at low and medium temperatures.

The following dyes act equally on wool and silk at boiling-heat:—Fast green, bluish mark (By.), patent blue, alkali blue, alkali violet, navy blue B (B.A.S.F.), acid violet 6 BN (By.), fast acid violet A2R and 10B (M.L.Br. and By.), Bengal-rose (dyed with acetic acid), anthracite black (C.), naphthylamine black D (C.), etc. The following have a rather stronger affinity for wool: light green S, wool green (B.A.S.F.); the acid orange dyes, like orange II; a few ponceaus, like palatine scarlet (B.A.S.F.), brilliant croceine (C.), etc.

On the basis of their affinity for silk and wool, the acid dyes may be divided into three groups, those given above as having an almost identical affinity for both fibres being taken as the first group. To a second group belong such dyes as chiefly dye wool when applied at boiling-heat, *e.g.* acid green, extra conc. (C.), tartrazine, orange G, a few ponceaus, as mark 2R (M.L.Br.), S. pat. (C.), indigocarmine cyanine (M.L.Br.), etc. Finally, the third group comprises the dyes having more affinity for silk than for wool at medium and low temperatures—azocarmine (B.A.S.F.), acid violet N (M.L.Br.), fast acid blue B (By.), water blue, etc.; as also the majority of the basic dyes, such as methyl green, auramine, rhodamine, etc.

The best means of dyeing wool and silk to equal shades is by using the dyes of Group I., unless prevented by other reasons such as their equalising properties, suitability for combination, etc. The *modus operandi* is as follows:—The bath is set with about 10 per cent. of "tartar preparation," bisulphate, and one-half the necessary quantity of dye, the goods being then entered and the bath raised to boiling-heat as quickly as the equalising properties of the dye permit, boiling being continued until the wool appears sufficiently shaded. The silk will, as a rule, be less deep in colour; consequently, after cooling the bath down to 45–50° C., the rest of the dye is added, and the operation continued in the cooling bath until the silk has been properly dyed. If, however, this result fails to ensue, recourse must be had to a suitable dye of the third group. In this manner a light yellow may be obtained with azoflavine, which, however, turns dirty in dark shades; a dark yellow and

orange, with orange II; red, with azocarmine, magdala red, or a ponceau; pale blue, with patent blue; dark blue, with acid violet 6BN and bluish fast green; black, with anthracite black, deepened with orange and a basic green at low temperature. For mode colours, use is preferably made of azocarmine, patent blue, and azoflavine.

To produce "shot" effects, the following procedure is adopted:—The wool is dyed first with a dye of the second group, at boiling-heat; the small amount of dye that has become fixed on the fibre of the silk is then removed by boiling with water, soap, or ammonium acetate, and the silk afterwards dyed in a third bath containing a dye of the third group, the bath being concentrated and cold, or, at most, lukewarm. Red, for instance, is produced on the wool by the aid of ponceau 2R, and the silk dyed green with methyl green and auramine; or the wool dyed green with acid green extra conc., the silk red with rhodamine, etc.

The most beautiful effects can be produced in this way, but the following points must be borne in mind:—(1) The dyeings on the two fibres must be as nearly equal in intensity as possible, and complementary; (2) the silk must be thoroughly freed from colour after the first dyeing; (3) the dyes employed in the third bath must have a low affinity for wool. These conditions, however, are rather difficult to carry out in practice, and, moreover, the three baths render the operation very troublesome; consequently, the general procedure is to first dye the wool with dyes of the second group, then cool the bath as much as possible, and dye the silk with dyes of the third class.

V. Sample Dyeings; Colorimetric Determinations; Reactions of Dye-Stuffs on the Fibre; Tests for Fastness.

Sample Dyeings and Colorimetric Determinations.

The determination of the value of dyes is made by sample dyeings or by means of the colorimeter, though in either case all that can be done is to effect a comparison between two or more samples of one and the same dye, or two or more very similar dyes. In both cases it must be borne in mind that minute differences in the intensity of two dyeings can only be detected in light shades. The greatest difficulty is encountered in examining yellows, and therefore in this case it is advisable to combine the dye in question with another dye of suitable character, *e.g.* a blue.

Sample Dyeing consists in making comparative dyeings with two or more parcels or samples of one and the same dye under

closely identical conditions, and examining the resulting colours for their relative intensity, shade, and purity. With this object a small quantity, say 1 grm., of each sample of dye is carefully weighed out and dissolved in 1 litre of water, each solution being then employed to dye equal weights of yarn in baths of otherwise identical constitution, and all under the same conditions of temperature. The best method of applying heat is to immerse the dye-baths in a heated strong brine. When mordant dyes are in question, the various samples of yarn must be mordanted beforehand in one and the same bath. Already during the process of dyeing it will be easily seen whether any considerable differences exist between the various samples, and should this be the case the weaker bath must be strengthened by adding sufficient of the dye solution to bring the dyeings into a condition of equality. It will also become apparent during the dyeing whether the dyes are homogeneous or mixtures, since the different dyes never draw on to the fibre so uniformly and simultaneously as to render the detection of a mixture impossible.

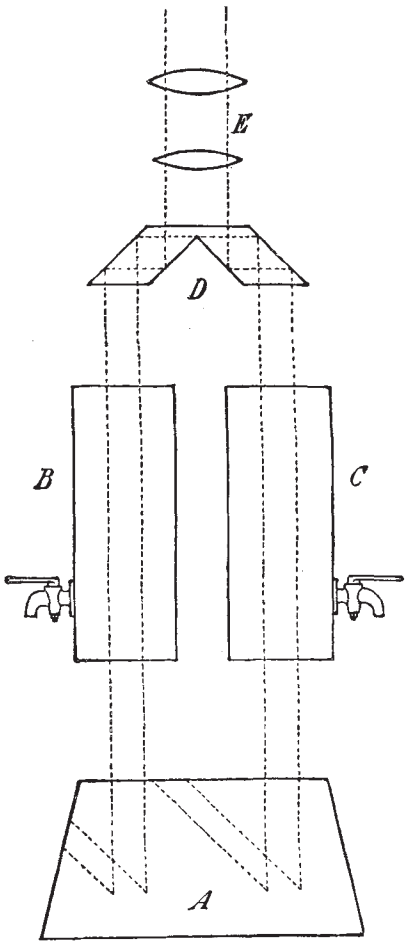

FIG. 35.

After dyeing, the samples are washed, dried, and the resulting difference determined with reference to the amount of dye consumed. At the same time it will have to be ascertained whether, through unequal heating, the one bath has become more highly concentrated than the other. Should this prove to be the case, the test must be repeated, since more dye is taken up from concentrated baths than from those more dilute. If the baths have been imperfectly exhausted, another dyeing with fresh yarn will give an idea of the quantity of dye left behind the first time.

A simpler, quicker, and more accurate method is afforded by the colorimeter. Of the various types of this instrument, mention need only be made here to that of C. H. Wolff, the construction of which is based on the fact that light rays suffer a diminution in brightness in passing through a stratum of coloured liquid, the decrease being in proportion to the degree of concentration of the liquid, *i.e.* the greater the quantity of dye in the liquid, the more will the light be dimmed in passing therethrough.

The accompanying sketch (Fig. 35) will facilitate description of the Wolff colorimeter :—

B and *C* are cubed cylinders into which the dye solutions are poured; *A* is a reflector; *D* a pair of prisms, which so unite the two bundles of light rays in the field of vision of the lens *E* that the one-half of the circular field of vision corresponds to the light transmitted through the one prism, and the other half to the rays traversing the other prism.

The two solutions for comparison, which must be very dilute, are placed in the respective cylinders and examined, the darker one being reduced in volume by drawing it off through the lateral tap until both sides of the field of vision appear of equal intensity of colour.

Now the capacity of absorption for light is inversely proportional to the thickness of the absorbent layer traversed by the rays. Thus, for example, if to produce equal intensity in the two halves of the field it is necessary to reduce the one liquid to half the volume of the other liquid, then the absorptive capacity of the former will be double that of the latter. As, now, the absorptive capacity of a liquid for light depends directly on the degree of concentration, then, by assuming the height of the two columns of liquid in the test cylinders as being represented by $H\ H'$, whilst the concentration of the liquids is expressed by $C\ C'$, we obtain the following simple relation :—

$$C : C' = H' : H.$$

The relative colour strength of the solutions under examination can be easily calculated by the aid of this proportion.

In making a determination it is not advisable to confine the examination to a single test, but to make at least two, and repeat these after reversing the two cylinders, the arithmetical mean of the four tests being taken to express the result.

Reactions of Dye-Stuffs on the Fibre.

In practice it is frequently desirable to ascertain what dye has b een employed to produce a given dyeng, and with this object the sample is cut into strips which are then subjected to the action of

various reagents, such as acids, alkalis, alcohol, etc., in order that some conclusion as to the nature of the dye can be drawn from the colour-changes ensuing therefrom. Owing to the large number of existing dyes this method is by no means easy, and, especially in the case of mixtures, is often only partially possible. For the assistance of the dyer, various tables, setting forth the necessary indications, have been drawn up, *e.g.* by Lehne and Rusterholz (Lehne's *Färberzeitung*, 1890, pp. 186, 226, 260, 318, 388; 1891, pp. 168, 276, 358; 1892, pp. 50, 198, 248, 332; 1893, pp. 216 254, 350; 1894, p. 22) and by K. Schimke (*Centralblatt f. Textilindustrie*, Berlin, 1892, pp. 6, 65, 108, 140, 198, 228). When, by the aid of these tables, the experimeter believes he has detected the dye used, he then makes a sample dyeing with the said dye-stuff on a similar fibre, and tests the resulting colour with the same reagents as before in order to ascertain the points of resemblance or difference.

Testing the Fastness of Dyes.

Fastness in dyes is a quality of equal importance with cost and colour, and a dye can only be considered as really fast when it proves capable of resisting for a sufficiently long time, without appreciable alteration, the influences to which it will be subjected in practical use.

It is not essential that a dye should be fast in every respect. For example, in the case of clothing, all that is required of a dye is that it will stand the various influences to which it will be exposed in wear; in the case of curtains, fastness to light is a prime essential; whilst the dye on underclothing, worn next the skin, must be able to withstand friction and perspiration.

Tests for fastness, however, never furnish more than relative values, and consequently these tests are best made in comparison between at least two dyes, or their dyeings, simultaneously—a necessary condition being that the dyeings in question shall be of as nearly equal intensity as possible.

Fastness to Light implies the power of a dye to withstand the combined influence of light and air. The chemical reaction that goes on during the fading of a colour has not been minutely examined, all that is known being that, in the absence of air, the influence of light is considerably reduced.

The fastness to light of any given dye depends on several circumstances, *e.g.* on the nature of the fibre, the method of fixing, and the intensity of the dyeing. Thus, dyeings on wool are mostly faster to light than those of the same dyes on other fibres;

whilst, in the case of logwood dyeings, the colour is faster when consisting of an iron or copper lake, the alumina and tin lakes being fugitive; the basic dyes are generally much faster to light when fixed with tannin or tartar emetic than with oleic acid, on cotton. Finally, as regards the intensity of the dyeing on the fastness to light, it is evident that a dark shade containing a larger quantity of dye will be able to stand the influence of light a far longer time than a light dyeing, not to mention that under the latter circumstances a slight change—especially of a qualitative nature—is more readily detected than in dark shades. Thus when, for example, a blue dye has the tendency to become greener in the light, this faculty may pass entirely unobserved in the case of dark shades, whereas in light shades it may result in a complete modification of the colour.

The manner in which a colour suffers alteration is therefore an important point; when it merely becomes paler, without losing its brightness and tint, it is decidedly faster to light than one that suffers a change of tone in the same time.

In exposing dyeings to light, two other peculiarities become apparent: some dyes (*e.g.* indigo) rapidly becoming lighter at first and then remaining for a long time without further change; others again (*e.g.* picric acid, azo yellow, etc.) turn somewhat darker at first.

Two forms of apparatus have been constructed for testing the fastness of dyes to light, that used by Oehler being arranged so that a collecting lens directs the concentrated rays of the sun in a vertical direction on to the material. The other apparatus, that of H. Perger, is illuminated by the electric light. In applying the test it has to be remembered that the intensity of the action exerted by the light depends on several circumstances—the time of year, climate, weather, and, finally, the manner in which the exposure is made; consequently the tests in all cases must be comparative, and made with at least two dyeings at the same time. When the fastness of a dye is known, this can be taken as a standard and used for comparing that of another exposed under the same conditions. The dyed samples are laid out flat on a sheet of strong paper, the one half of the sample being exposed, whilst the other half is covered over by a piece of cardboard, and, being thus protected from light and air, serves for comparison. The samples are then exposed freely (not under glass) to the sunlight in a place where they are protected against dust and also against acid or alkaline fumes. The use of other sources of light, such as the electric light, gives different results, and therefore is not suitable for practical purposes. At the start the illuminated and protected

portions of the sample should be compared daily, and an incipient change in the colour must not lead to the abandonment of the test, it being necessary to further examine the progress of such change. Dyes that will stand exposure for a month in the summer without appreciable alteration may be considered as very fast to light.

Fastness to Water, Washing, and Milling, implies the behaviour of dyes under the action of water or solutions of soap; and the points to ascertain are whether the dye changes in colour or intensity, and if it bleeds into white or undyed fibre with which it is washed. The requirements exacted in this particular vary considerably, carpets, curtains, and upholstery stuffs for instance not being required to stand washing, as a rule; whereas yarns that are to be woven into pattern fabrics and then milled must remain entirely unchanged during that operation and exhibit no sign of bleeding.

In testing a dye for its fastness to water, a sample of yarn dyed with the specimen under examination is plaited along with a piece of white yarn and left immersed in cold water all night. To be quite fast, the dye must not dissolve in the water, and thus colour it, or bleed into the white yarn. In the case of woollen yarns this test is usually performed by boiling the sample in water for a quarter to half an hour.

Fastness to Washing and Soap is tested by plaiting a sample of dyed yarn with white yarn and then treating them for a quarter to half an hour in a solution of soap (about 0·2 per cent.) first at 50–60° C. and then at 100° C.

Fastness to Milling is required of woollen goods only, and is tested by subjecting the plait of white and dyed yarn to a rigorous milling by hand, with an alkaline soap, then washing and leaving to stand overnight in a rather wet condition. For the dye to be really fast, it is necessary that no staining of the white should occur, and also that the dyed sample remains free from alteration. The test will be still more severe if the sample be left for several hours in the soapy solution after milling.

In testing wool-dyeings for **Fastness to Acids,** the sample is carbonised with sulphuric acid and then neutralised. Cotton-dyeings are regarded as fast to acid when they will stand dyeing in an acid bath, as applied to wool, without suffering any appreciable alteration of shade or bleeding into white wool. With this object the dyed cotton is boiled along with white wool in a bath containing 4 per cent. of sulphuric acid and 10 per cent. of Glauber salt (calculated on the weight of the wool) for an hour. This test serves to determine whether a given dye is suitable for use on

cotton that is to be woven along with animal fibre which is afterwards to be dyed in an acid bath in the piece.

Fastness to Perspiration is tested by immersing the sample for an hour, in association with white cotton and wool, in a $2\frac{1}{2}^{\circ}$ B. solution of acetic acid at 40° C.

Fastness to Bleach (chemicking) is tested only in the case of cotton, the dyed sample being steeped for an hour in a cold 1° B. solution of bleaching powder.

Fastness to Sulphur is a test applied solely to wool. The sample, plaited along with white yarn, is first soaped, squeezed, and then left for twelve hours in an atmosphere of sulphurous acid.

Sometimes, and especially in the case of wool-dyeings, a quicklime test is imposed, the stuff being padded over with a pulp of slaked lime, left to dry, and examined for alteration after brushing off the lime. This test, as well as sprinkling the stuff with soda solution, followed by drying, is performed when information is desired as to the capacity of the dye for standing the influence of street mud.

Fastness to Ironing and Steaming is tested by subjecting the dyed sample to hot ironing or drying on a surface of heated metal, and by steaming. The dye should either be quite free from alteration or else resume its original shade after a short exposure to the air. In applying these tests it must not be forgotten that the wool itself may assume a yellowish tinge under excessive steaming, the result being an apparent alteration of some colours—blue, for example. For the sake of comparison, it is therefore necessary to steam an undyed sample of the same material at the same time.

CHAPTER V

PRINTING[1]

WHEREAS the object in dyeing is to secure uniform and complete coloration of the entire material of the fabric, the purpose of the printer is to apply the colouring matters only in certain parts and in a well-defined pattern; hence, printing may be regarded as local dyeing. Closely allied, however, as these two branches of the subject may be, it follows from the nature of the case that the ways and means whereby their respective objects are secured must be very different. For instance, in dyeing, it is for the most part feasible to modify a dyed colour by the subsequent application of other dyes; but in printing this is not possible, and therefore all the materials employed must be carefully examined before use.

For the application of dye to certain parts of a fabric, and according to a well-defined pattern, recourse must be had to an application unknown in the dyeing process, namely, a printing block or forme, by means of which it becomes feasible to print any dissolved dye upon the fabric. It is, however, evident that although the dissolved dye may be printed as a well-defined pattern on the fabric, the contour of the design would very soon lose its sharpness of outline, owing to the running of the solution; and to prevent such an occurrence a further adjunct, rarely if ever used in dyeing, has to be called in aid, namely, an agglutinant, or thickening material, with which the colour is incorporated before application. Apart from this, the colour has to receive other additions, and also to be subjected to certain after-treatments, which will be dealt with later on.

Besides direct printing, there are other means whereby a coloured pattern can be produced in cloth-printing. Thus, if a fabric be printed over with substances that are impervious to liquids, and is then dyed, it follows that the dye will be fixed only on the unprinted

[1] The author is indebted for much of the information contained in this chapter to the handbooks on Calico-Printing by Lauber and Sansone, and the article on Printing, by Stork and Benade, in Karmarsch-Heerens' Technical Dictionary, to which sources the reader is referred for points of detail, especially as regards the compounding of the printing materials.

parts of the fabric, the printed portions being left white when the goods have been washed. This kind of printing, whereby white figures can be produced on a coloured ground, is known as "reserve printing," and the substances employed to protect the printed portions from the action of the dye are called "reserves."

Again, it is possible to produce white figures on a dyed material by printing it over with substances that destroy or discharge the colour. This is the so-called "discharge printing."

By the assistance of reserve and discharge printing it is possible to produce patterns in two ways: either a mordant is added to the reserve or discharge before printing, and the goods afterwards dyed, whereby the discharged or reserve portions become coloured because of the mordant there situated; or the reserve or discharge is incorporated with a dye, and then printed. Finally, as a third method, the fabric may be printed with a mordant, which is then fixed in a suitable manner, and the goods dyed, whereupon only the mordanted portions will retain the dye, leaving the rest white, the method being thus a combination of printing and dyeing.

Historical.—From the very earliest times the peoples of the Orient have practised the art of cloth-printing; and although the work was performed in a highly primitive manner, the above-mentioned methods of producing coloured patterns would seem to have been known to them.

The most primitive state of transition between dyeing and printing is found among the Chinese, who are known to produce coloured figures on cloth by hand painting.

The true home of the cloth-printing industry, however, seems to be India, printing blocks for the production of coloured designs having been in use there from the most ancient times. Reserve printing must also be classed as an Indian invention; and to this type of product belongs the so-called "Battik" goods that are still produced in Sumatra and Java, the design being drawn on the goods by the aid of a mixture of resin and wax, which are applied in a melted state, and, after solidification, form an impenetrable reserve, so that the parts thus covered remain undyed when the fabric is afterwards dyed (usually by vatting). On subsequently removing the reserve by hot water, there appears a white design on a coloured ground.

This method was first brought into Europe by the French, from their colonies in Eastern Asia, as the so-called "porcelain-printing" (white on blue ground).

The first calico-printing factory on record was established at Richmond-on-Thames in 1676 by a French refugee; later on, works were started at Neuchâtel (1689); in several German towns

—Augsburg, Heidenheim-on-Brenz; at Sainte Suzanne, in France; in Austria (Bürgstein, Schwechat, Friedau, Kettenhof, Kosmanos), etc.

At first hand-presses were employed, the design being deeply engraved on a copper plate, which the printer covered with colour by the aid of a brush, the excess being afterwards removed with a knife. When thus ready for printing, the plate was raised by the mechanism of the press, brought into contact with the material to receive the impression, and then returned to the first position, for re-inking.

This method is cheap, and gives a sharp impression. It is still employed—in Switzerland, for example—generally for broad designs, and chiefly for silk kerchiefs.

At a later period other machines were introduced, the most important being the Perrotine (invented by Perrot of Rouen, in 1834), which can also be used as a multiple-colour machine. The "Hexe" press is still to be found in a few cloth-printing works. At present, however, the cylinder printing press, first introduced by Bell in 1785, is the most widely used of any.

Hand Printing.

The printing plates used must not be too large or too small, the former defect meaning excessive weight and trouble in handling, whilst in the other extreme the work takes too much time.

The material for the plates must be durable and not easily warped, choice being therefore made of pear-, beech-, and box-wood, thin boards (about one inch) of which are glued on the back of similar boards of oak or beech, which in turn are backed by blocks of pine, the latter being recessed so as to hold better. The boards must be arranged so that the grain runs in different directions, in order to minimise the tendency to warp. The under (free) side of the first piece of wood is planed smooth.

To transmit the pattern to the block, the designer divides the pattern by horizontal and vertical lines, so as to include within the marked-off portion all the elements of the pattern, these lines being then transferred to the chalked block. The design is next traced with pencil and paper, the tracing being then laid face downwards on the marked block, and the reverse is rubbed over with a hard, smooth tool, the impression being afterwards touched up by hand. As each block can only be used to print one colour at a time, a separate block must be used for each differently coloured portion of the design.

The tracing of the pattern is never so large as the block, and must therefore be transferred as many times as are necessary to cover the surface of the block. Where the repetition of a small

pattern is in question, a small model is often made, the impression being repeated on the block until the entire surface is covered. To ensure accuracy of position, use is made of register pins, which are placed on both sides of the printing block, and in applying the latter, care must be taken to see that the pins on the left side exactly coincide with the marks left by those on the right-hand side during the previous impression. In succeeding rows, the upper pins must register with the marks left by the lower pins.

The design thus transmitted must be brought into relief by punching the wood with steel punches. Where the printing surfaces are large, it is a frequent practice to merely punch the outlines and fill the intermediate space with felt, which substance absorbs the colour much more uniformly than wood and therefore prints better.

Fine details cut on wood are liable to rapid wear, and are therefore generally done on copper or brass inlaid in the wood block. Frequently, however, the entire surface of the printing forme is of metal, the design being imparted by casting. For this purpose a perfectly dry block of lime-wood, cut crossways of the grain, is taken, and punched with the design, which in this case is hollowed out, the lighter details being burned out by means of heated steel dyes pressed against the wood until the impression has reached a certain depth. The contours of the larger and heavier parts of the design are cut. This done, the hollows are filled with pieces of brass so that the metal projects a few millimetres above the surface of the block, and a molten alloy of tin, lead, and antimony is then applied, which envelops the brass and transmits sufficient heat to the depressions in the wood to carbonise the surface, which is thereby smoothed and deprived of the tendency to shrink. Thereupon the brass is removed, and the resulting wooden matrix or mould is used for making the cast. The casting is trimmed smooth with the file and nailed on to a wooden backing.

Other appliances required for printing with the hand-press are a frame and ink-duct, the former consisting of a strong framework supporting a planed block of hardwood, the dimensions of which vary according to the class of work to be done,—a narrow block being needed for long fabrics, and a wide one for kerchiefs. This block is covered with a tightly stretched layer of flannel (printers' blanket), serving as a soft backing for the goods.

On one of the narrow ends of the frame is an arrangement supporting the roller from which the goods to be printed are unwound. The goods issuing from the press are carried over guide rollers, either on the ceiling of the printed room or underneath the frame, for the purpose of drying the printed colour.

The ink-duct is a rectangular trough, about twenty inches long and wide, and ten inches deep, which is filled about half-full of starch paste, for the purpose of forming an elastic bed, upon which is laid a piece of oilcloth stretched on a frame into which fits a second frame carrying a stretched cloth, the colour being spread out on this last by the aid of a brush as evenly as possible.

To begin printing, the end of the cloth is laid on the press table and marked with a ruler and pencil, to show where the block is to be applied the first time. The block is then brought into contact two or three times with the inking-pad, and then applied to the cloth, a few blows with the mallet forcing the colour into the material; which done, the block is removed, re-inked, and applied again. In this second and all succeeding applications the block must be made to register by means of the aforesaid register pins, which should be situated in such a position that their impression, though visible to the printer, forms part of the coloured design.

In multiple-colour printing, the work is begun with the block giving the most comprehensive idea of the whole design.

In printing "squares," the fabric is first divided by lines indicating the limits of each square. The blocks for this work are mostly arranged to print one quarter of the whole square.

Some colours must be printed warm, for which purpose the inking-pad must be set on hot bricks or immersed in hot water. When readily oxidisable colours are used, they should be stored in the lower part of the inking-pad instead of the starch paste, and be covered over with a porous cloth.

Unless the cloth be kept on the stretch whilst on the press table, it will shrink, both in length and breadth, in the drying, and thus prevent the last-applied colour registering with the previous ones. To obviate this difficulty the colours must be applied in succession as quickly as possible, or else the fabric is stretched in both directions after printing each colour.

Full shades cannot be printed on thick fabrics by the hand-press. The method is specially suitable for the production of multiple-colour printings and for very wide goods, since to employ mechanical presses for these classes of work would necessitate the use of very complex or wide, and in either event very costly, machines. Hand printing is also superior to the machine-press, inasmuch as it does not dirty the white.

The Perrotine Press.

The Perrotine press is a machine for printing from cast-metal plates carrying the design in relief, and resembles the hand-press

in its points of superiority over the cylinder press. The number of colours, however, that can be printed in this press is limited, and it is now used to only a very small extent. A three-colour Perrotine press is shown, as a diagrammatic sketch, in Fig. 36.

Here *a* is the backing cloth, forming an elastic support for the goods; *b* is a piece of unfinished cotton cloth, to keep the backing cloth from being dirtied by the printing colour; *c* is the cloth to

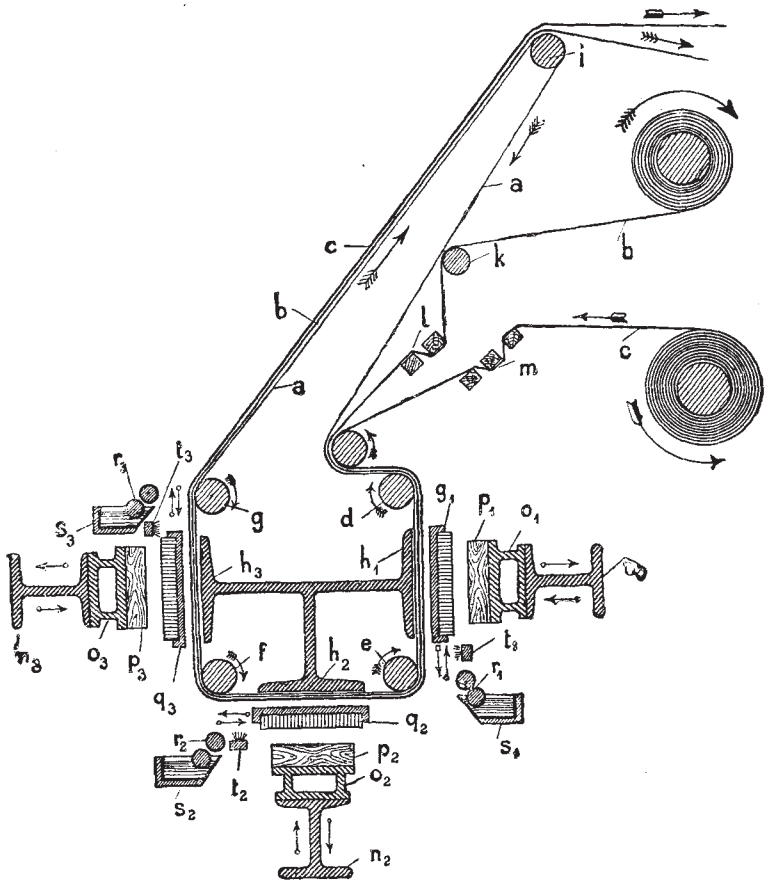

FIG. 36.

be printed; h_1, h_2, h_3 are the printing tables, furnishing the solid backing. The slides n_1, n_2, n_3, which move in the direction of the arrows, and carry the block-holders o_1, o_2, o_3, press the blocks p_1, p_2, p_3 alternately against the inking pads q_1, q_2, q_3, which themselves have a reciprocating motion at right angles to that of the blocks. At the moment the blocks are withdrawn from contact with the printed surface, the pads are moved so as to pass by the pairs of

rollers r_1, r_2, r_3, which in their rotary motion take up the colour from the ducts s_1, s_2, s_3, and pass it on to the pads, where it is smoothed level by the brushes t_1, t_2, t_3. The slides next advance and press the blocks against the pads, then retreat, and, after the pads have been moved slightly to one side, again press the blocks on the pads. The impression then follows immediately, during which operation the pads are moved over the inking rollers. After each impression the backing cloth, intermediate cloth, and cloth to be printed are moved forward a distance corresponding to the exact breadth of the block, so that the goods are fully printed by the time they pass away from the third block. If desired, the advance of the goods can be stayed, and the movement of the printing mechanism continued, the impressions being in such case repeated in exactly the same place as often as required.

The Cylinder Press.

In the cylinder machine the impression is produced by means of engraved rollers, known as copper rollers, though they really consist of an alloy resembling bronze. They are in the form of a hollow cylinder, into which are forced a wedge and a steel spindle carrying a pinion by means of which the cylinder is set in motion.

In this case, therefore, it is necessary for the goods to be pressed into the depressions of the cylinder, in order to take up the colour; hence a heavier pressure is needed than in the case of the hand-press, and the machine must be driven by power—a condition lying at the root of the high productivity of the cylinder press, and one that renders it the sole class of machine suitable for the production of printed goods on a large scale. This press exhibits the further advantages of giving a sharp impression and perfect register in the case of multiple-colour patterns.

The cylinder press may be of either the single-colour or the multiple-colour type, and each press is driven by its own motor.

A single-colour machine will print up to 180 pieces of 60–70 yards each per diem of ten hours. With multiple-colour machines the working speed is much slower, a twelve-colour machine, for instance, only printing about forty pieces a day.

Engraving the Printing Cylinders.—As already mentioned, the design is engraved on the cylinders. In order to hold the colour better on broad parts of the design, the surface there hatched with V-shaped channels, or punched with conical stipples.

The engraving of the design is effected in various ways. The method apparently at first sight most suitable—namely, to trace the design on the surface, and then cut it out with the graver—is really

the one least in use, and then only employed for the outlines when the portions of the design to be engraved are so large that they do not repeat, or only partly so.

In all other cases, *i.e.* when frequent repetitions of the same figures occur, a small steel roller is prepared, by means of which the pattern is pressed into the surface of the cylinder, the roller being in relief.

The engraving of the cylinder is frequently effected by etching, either alone or in conjunction with the foregoing method. For this purpose the cylinder is coated over with asphalt lacquer, the lines of the pattern being then drawn in the asphalt so as to expose the underlying metal, after which the cylinder is immersed in dilute nitric acid, which etches out the exposed parts and leaves the design engraved on the metal.

The sole decisive factor in the choice of methods is speed. Most frequently the work is done by the aid of a steel roller or "molette," on which the design is formed in relief by the following indirect process, the direct method being too difficult to attempt. For this purpose a steel cylinder of very good quality and suitable length is exposed to red heat for about twelve hours, embedded in a mixture of powdered charcoal and chalk, and placed in an iron box surrounded with loam. It is then covered with ashes and left to cool very slowly for two to three days, whereby the steel becomes soft, and is afterwards turned and polished to the exact size required, *i.e.* until its peripheral measurement is equal to the width of the pattern. The next step is to clean it by scrubbing with lye, levigated chalk, and dissolved soap, followed by a short immersion in a dilute solution of copper sulphate, rinsing, and drying. To transfer the design to this cylinder, a tracing of so much of the pattern as will be printed of the one colour is made upon satin paper, rendered transparent by impregnation with a solution of gum dammar in turpentine, the tracing ink employed containing sodium sulphide. This tracing is wound on the cylinder, fastened thereon, and left for a quarter to half an hour, by which time the design will be developed by the formation of copper sulphide on the surface of the cylinder. The lines thus marked are cut with a steel graving tool shaped like a slightly bent prism of rhombic section and ground off a slant at the end, thus leaving the convex edge of the prism to terminate in a projecting point. After the outlines have been cut out the conical stipples are punched to a certain depth in a machine, then deepened by hand with a hammer and punch, and finally bored out. They must be set at equal distances apart, and in rows of uniform direction. The hatching is effected with double cutter gravers, the one cutting edge working

in the groove already formed, whereby perfect regularity in the position of the hatched lines is secured. Mostly, however, the hatching is produced by etching, the lines being drawn on the asphalted surface by means of a ruling machine. They must be always arranged spirally, and not parallel to the axis of the roller, or they would catch in the ink knife in the operation of printing. Cross hatching is generally employed. When the entire design is composed of hatchings or stipples, the rollers are termed padding rollers, the cloth being printed over its entire surface with a uniform layer of colour, and not in a figured pattern.

The engraving of this roller is conducted under a magnifying glass, the roller being mounted so as to rotate on the graving frame. When the process is completed the roller is polished with fine-grained sandstone and oil, and is punched with a number of coarse stipples outside the limits of the design in order to prevent slipping during the subsequent pressure. It is then hardened by embedding it in spodium paste in the same box that was used for the softening treatment, heated to pale redness, and quickly plunged into cold water several times in succession. As the roller, if too hard, would be liable to spring under the subsequently applied pressure, it is tested with chisels of different degrees of hardness, and, if found too hard, is rendered a little milder by reheating. Finally it is scoured with loam and water, rinsed, and dried.

To produce the actual stamping roller, with the design in relief, from this molette, a steel cylinder, the peripheral measurement of which is a multiple of the first one, is softened, the two being then pressed tightly together by the aid of screw clamps and set in rotary motion. During this operation, whereby the metal of the softened cylinder is forced into the depressions of the hard one, the cylinder is strewn with a mixture of resin, fat, and wax. This mixture is also forced into the depressions of the matrix, and spreads thence over the raised portions of the patrix, so that when the latter is immersed in nitric acid only the unprotected parts are corroded by the acid, the result being to deepen the cuttings. The molettes are again clamped together and pressed, followed by another etching, the series of operations being repeated until the desired effect is completely produced. The stipples designed to prevent slipping are next cut away with hammer and chisel, and their place taken by shallow depressions serving the same purpose.

The finished patrix should be a little thicker in the middle than at the ends, because the latter always wear away quicker, and for this purpose the ends are tapered off by a succession of etchings, commencing at the extremities, after which the roller is finally hardened.

This roller is now employed to transfer the pattern to the actual printing roller, which must be turned down so as to exactly correspond to a multiple of the molette, and is then mounted so as to rotate on its axis, clamped in contact with the molette roller, and set in motion, slowly at first, but more quickly afterwards, plenty of oil being applied. When the design has been cut all round the printing roller, the molette is shifted by a distance exactly corresponding to the length of the pattern, and clamped on again, the whole series of operations being repeated until the full working width of the printing roller has been treated. The projecting portions are then ground smooth, and the roller is cleaned.

It being necessary that the ink should be removed as completely as possible from the raised portions of the cylinder, the surface of the latter must be absolutely true, since the colour would otherwise collect in any irregularities—other than those of the pattern—and dirty the fabric. To produce this perfectly plain surface the cylinder is slightly etched with nitric acid and then lightly ground, which will reveal the projecting portions by the contrast between their smooth surface and the dulness resulting from the etching. These prominences are removed by etching, the hollows being lacquered over and the cylinder dipped in nitric acid. Finally, the whole cylinder is gently ground. Faulty engravings, as well as old patterns to be replaced by new ones, are removed entirely by grinding.

Engraved designs can be produced on the molette or the printing cylinder entirely by etching. In the first place, the design is brought, by means of a camera obscura, in a five-fold state of magnification, on to a varnished zinc plate, and the details painted in their natural colours in order to facilitate recognition of the parts which are in association and have to be transferred to the same roller. The outlines are then punched out, their dimensions being diminished in a degree determined by experience, because of the tendency of the acid to enlarge them in the etching process. The reduction of the magnified design to its original dimensions in the course of transfer to the printing roller is effected by means of the pantograph, the stylus of which is moved over the outlines on the zinc plate, whilst the diamond engraving point which marks the pattern on the lacquered printing cylinder has an amplitude of movement only one-fifth that of the stylus. A sufficient number of these diamond points is provided to mark the pattern over the whole length of the printing roller at one operation. The roller is then etched in the usual manner, the lacquer washed off, and the etching gone over with the graving tool.

In printing on the cylinder machine the cloth suffers extension mainly in a longitudinal direction, the stretching progressing at each roller, so that on reaching the sixth roller it has attained about one-sixteenth of an inch. In order to counteract this tendency the rollers are made of different sizes (diameter); thus, in a four-colour machine, the first roller is a little smaller than the second and third (which are equal), whilst the fourth and last are a little larger than the intermediate ones. The disadvantage of this method is that the serial order in which the rollers come into action is arbitrarily fixed beforehand. In some works, rollers of equal diameter are used throughout, and the stretching is counteracted by special means, which, however, are not divulged by the users.

Setting and Working a Single-Colour Cylinder Machine.

The chief parts of the single-colour cylinder printing press (Fig. 37) are as follows: (*a*) the engraved printing cylinder; (*b*) the backing cylinder; (*c*) the ink-duct; (*d*) the inking roller; (*e*) the scraper; (*f*) the heating or drying plates.

In this figure the goods to be printed are indicated by *g*, the backing cloth by *i*, and the intermediate cloth by *h*. The path taken by the goods is shown by the arrows, the cloth being unwound from the roller *k*, passed between the printing and the backing cylinders, where it is printed, and then led alternately upwards and downwards between drying plates, or dried by circulating through an enclosed hot chamber (*o*), and finally delivered in folds at *l*.

Successful printing depends on several points of detail, including chiefly — a properly compounded printing colour and well prepared printing cylinder being presupposed—the accurate working of the scraper. As already stated, this organ serves to scrape off the colour from all the unengraved parts of the cylinder. It consists of a thin steel blade which is pressed against the printing cylinder, in the direction of rotation of the latter, by means of a weighted lever placed on one side, and receives a reciprocating motion by the action of an eccentric rod actuating a bell-crank lever. The upper edge is ground sharp, though in some cases (*e.g.* striped patterns) a rounded edge is preferred. When acid colours are used, the scraper must be protected by a coating of varnish. In some cases a second or counter scraper is provided (*m*, Fig. 37), mounted in the opposite direction to the movement of the cylinder, its use being to remove any fine nap that has become separated from the fabric, and prevent the same from getting into the colour; this scraper is immovable.

The backing or pressure cylinder serves as a solid abutment for the printing roller. To make this pressure elastic, the backing

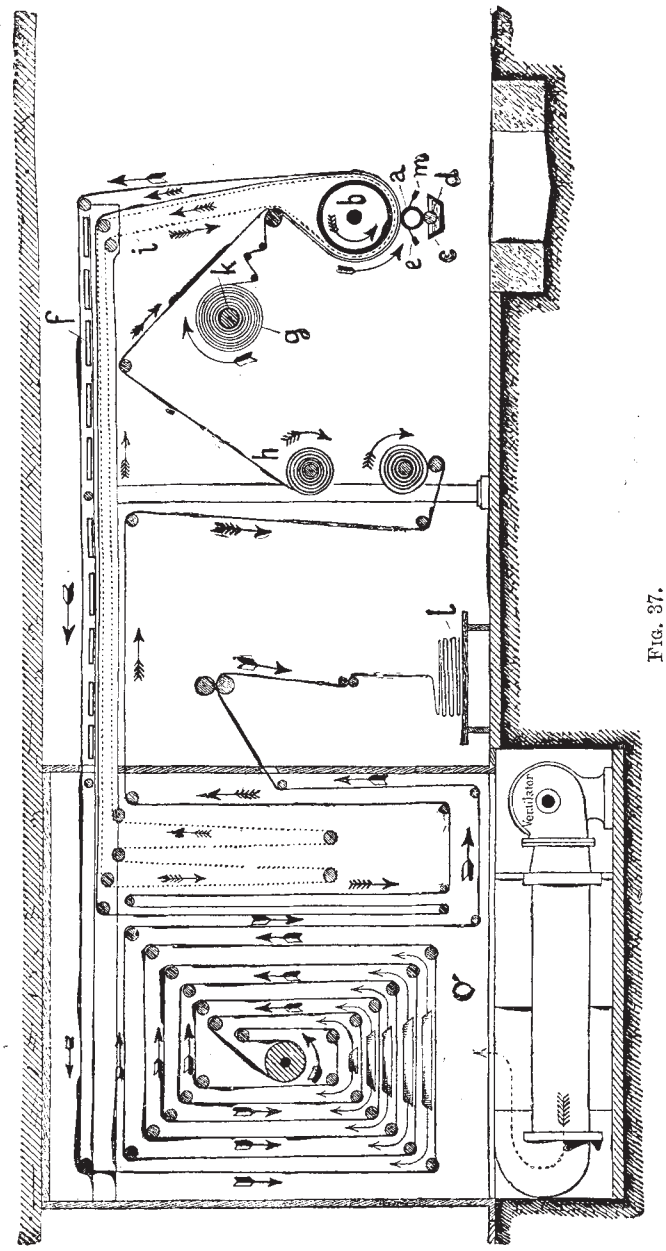

FIG. 37.

cylinder is mounted in adjustable bearings, which can be moved up and down in grooves by the aid of a train of levers, the pressure on

the printing cylinder being increased at will by weighting the levers. The necessary accurate parallelism of the two cylinders is secured by the aid of strong screws, and the elasticity of the pressure is increased by covering the backing cylinder with several layers of tightly stretched printer's blanket. The same object is effected by the backing cloth (*i*, Fig. 37), an endless cloth composed of several layers of stout cotton fabric fastened together with caoutchouc; in this case, as also in the blanket clothing the cylinder, all wrinkles must be entirely avoided. The intermediate cloth, which keeps the backing cloth from becoming stained by the printing colour, is of rough gassed cotton fabric, which after a while is cleansed by bleaching. It runs between the cloth to be printed and the backing cloth. After passing through the machine all three cloths are dried by being led between hot plates (*f*, Fig. 37), which are generally placed in the rear of the machine; or by circulating through a closed hot chamber. The intermediate cloth is afterwards washed and used over again; though a better way is to keep this cloth in continuous motion, washing it by passage through a water-trough and roller brushes, after leaving the press, and then drying it on a hot cylinder.

In printing, the printing cylinder is set in motion by toothed gearing, and carries the backing cylinder round with it. A piece of the intermediate cloth is first passed between the cylinders, and the extra piece, attached to the cloth to be printed, is also passed through and fixed on to the guide bands leading to the drying apparatus. Both the goods and the intermediate must be quite straight, free from folds, and passed into the machine at a certain tension, which is attained by applying weights to the axes of the rollers on which these cloths are wound, in order to ensure uniform pressure against the bearings.

The pull exerted by the two cylinders on the goods and intermediate cloth in order to unwind them from their respective rollers must never be so great as to damage the fabric, and should remain as uniform as possible during the operation of printing—an object attained by the aforesaid weighting.

The task of the printer consists in watching the fabric as it passes through the machine, so as to immediately detect any defects in the printing. This is arduous work, and requires the aid of a good light to perform successfully, on which account the machine is generally set up in front of a large window. As soon as the first yard has passed through the machine the printer must satisfy himself, by turning up the edges of the stuff, that the pressure is equal on both sides; the colour should show through at the back to an equal degree on both edges. The defects arising in printing

generally originate in the scraper. Thus, if any solid substance, for example, get between the scraper and the printing cylinder and lift up the former a little, the scraper will cease to act for that instant, and will thus leave a cross stripe of colour on the cylinder. Should the solid obstruction (*e.g.* a grain of sand) remain, the scraper will be prevented from acting on the colour at that particular spot, and a longitudinal stripe of colour will therefore be formed. Similar stripes are also produced when the scraper has become worn in places through constant friction against the engraved roller. If the edge of the scraper has not been ground sharp enough, the impression of the outlines will be fuzzy instead of clear. When the printing cylinder is not true, the scraper will not touch such parts as are below the general level.

Another cause of defective printing may reside in the colour, especially when this does not properly come off on to the cloth, but remains in part in the channels of the engraved surface. When such is the case, the inking roller must be replaced by a roller brush. In the case of colours, like chrome yellow, that exhibit this defect in a higher degree, a second stationary brush must be fixed up in front of the printing cylinder.

In any event, as soon as any defect in the printing is noticed, the printer must stop the machine and remove the cause. As the scraper is the chief cause of defects, this tool must be reground after a certain number of pieces have been printed.

When a change of colour is made, the printing cylinder, scraper, and ink-duct must all be thoroughly cleaned, the best plan being to keep separate sets of brushes and cleaning cloths for blue, red, and in fact for each different colour used.

Setting up and Working a Multiple-Colour Machine.

Although cloth-printing machines have been constructed to print as many as twenty, twenty-five, and even more colours, it is not usual to go higher than twelve, since the heavy pressure to which the fabric is exposed necessitates the employment of stronger colours (*i.e.* richer in pigment). The machines most frequently are two to six-colour presses.

The multiple-colour machine has a separate printing cylinder, ink-duct, ink-roller, and scraper, for each roller; a three-colour machine, therefore, having three printing cylinders, three ink-ducts, three inking rollers, and three scrapers. On the other hand, there is only a single backing cylinder, backing cloth, and intermediate cloth, as in the single-colour machine.

In this case the arrangement for producing elastic pressure is

somewhat different. The backing cylinder, the size of which depends on the number and size of the printing cylinders, is mounted on bearings that can be raised and lowered by means of screws, but it is kept fixed during printing. The set of levers mentioned in the single-colour machine acts in this case on the lowermost printing cylinder, the others being pressed against the backing cylinder, either by the aid of screws fitted with rubber rings or else by means of levers.

The principal difference in the method of working the two classes of machines consists in the method of producing the register, *i.e.* the proper relative adjustment of the various parts composing the pattern. For this purpose a special device is required,—the wheels mounted on the different roller spindles, which are driven

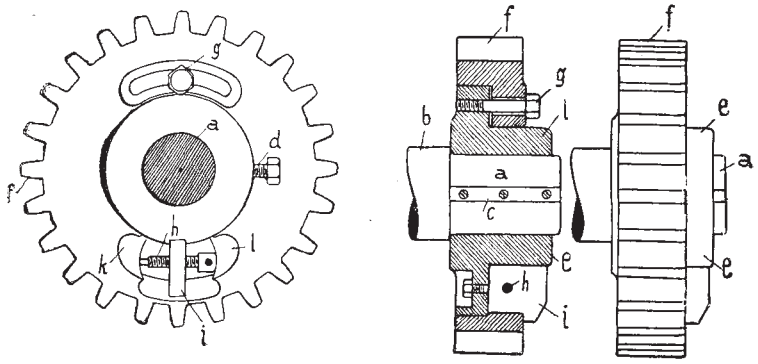

FIG. 38.

by a pinion in the centre, being fitted with a device which enables any difference in the movement and situation of the individual rollers to be compensated; these wheels are therefore called register wheels. A sleeve *e* is fastened on the trunnion of the printing cylinder *b* by means of the spring key *c* and set screw *d*, and is loosely connected with the driving-wheel *f* by means of the screw *g*. A screw *h* passes through the lug *i* on the sleeve *e*, and rests at both ends against two half-moon lugs *k l* on the printing cylinder wheel. On turning the screw in one or the other direction by means of a key-pin passing through the head (which can be done whilst the machine is running), the sleeve *e* is moved in an axial direction, and imparts a similar movement to the printing cylinder, so that in this way the rollers can be brought into register when either too far ahead or behind. It is, however, necessary to have the register approximately correct before starting, and this is effected in the following manner:—

The lower roller is first put into position and set parallel to the

axis of the backing cylinder, the other rollers being then put in and set parallel to the first. The cylinders having been marked by the engraver at the place where they correspond, that on the first roller is now marked with chalk, and the machine is started slowly, only the intermediate cloth being run through at first. This chalk-mark prints off on the intermediate cloth, and the resulting impression should exactly coincide with the corresponding marks on the other cylinders if the register is correct. This will rarely if ever be the case at the outset, and it will be necessary for the printer to adjust the register either by a lateral movement of the rollers or by means of register wheels. This having been approximately done, the ink-duct is filled with colour, and a remnant of cotton fabric is run through the machine, the resulting impression showing what additional correction is required to obtain a perfectly accurate register.

In beginning to print, the machine is first run very slowly; and the printer must give careful attention to all the points already mentioned in connection with single-colour printing; in addition to which he will have to look after the register all the time the printing continues, since slight alterations of register are constantly occurring, as a result either of slight modifications in the tension of the fabric, or from other causes. This work of adjustment can always be carried out while the machine is running, stoppages being avoided as much as possible, since they are liable to produce light streaks on the goods, in consequence of the colour running out of the engraved parts near the point of contact with the material.

An unavoidable inconvenience in multiple colour-printing on the cylinder machine is, that the colour cannot be completely removed from the smooth parts of the cylinders by the scraper, and consequently small particles of colour are left on the material, and get mixed with the next following colour. On this account great care must be taken to use the most delicate colours (*e.g.* pink, yellow, pale blue), first leaving those capable (like black) of doing most damage until last. To prevent a clouding of the colour by preceding colours, a so-called water-roller is placed between each two-printing cylinders. This consists of a smooth cylinder, provided with a scraper, and fed with a thin solution of tragacanth or gum. Sometimes the final printing cylinder is followed by a smooth cylinder, which presses the colour into the material, this being employed when it is desired to have the pattern on thin material shown up about the same on both sides, so that the corresponding parts exactly coincide, as in the duplex printing machines, which will print up to eight colours on each side, the method of working being shown in the diagrammatic sketch (Fig. 39).

Really the machine consists of two machines, each having its

own backing cylinder, backing cloth, and intermediate cloth. The engraving on the rollers of the one machine is to those on the other as image and reflection.

Before beginning to print the actual fabric, about thirty yards

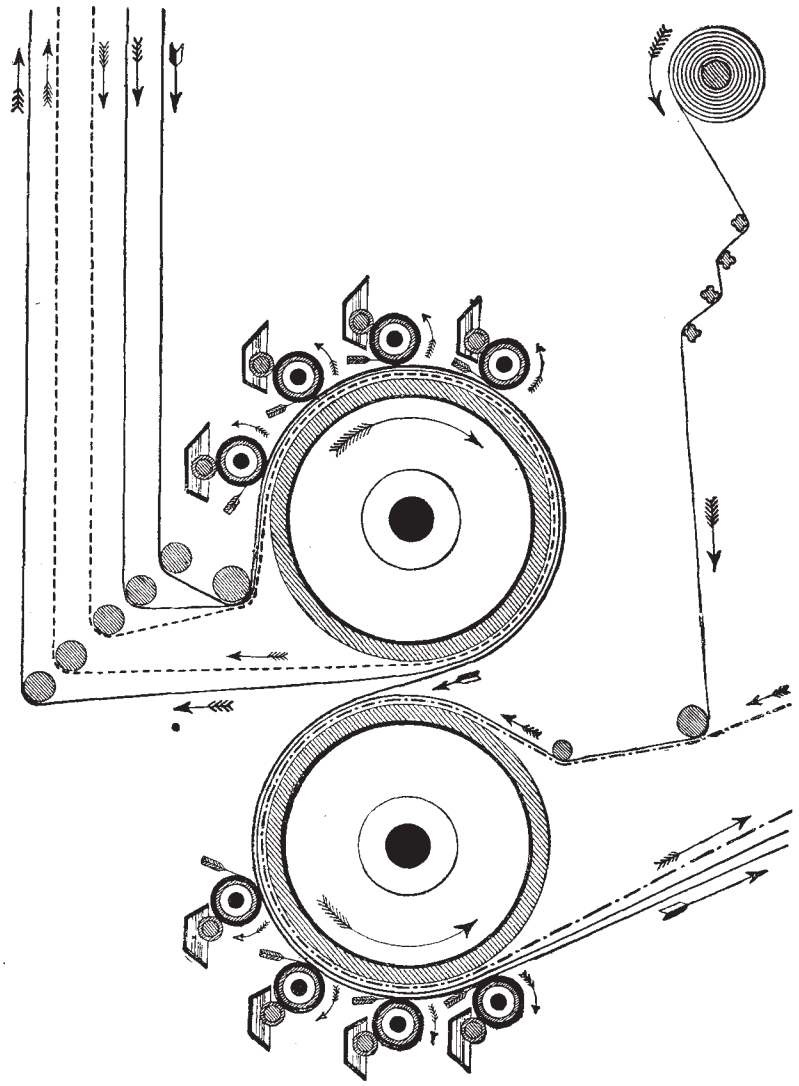

FIG. 39.

of material are run through the machine to enable the rollers to be adjusted and set in register. For the latter purpose all the rollers of each separate machine are coanected with a large register wheel, to that the whole of the rollers can be adjusted to the same extent

by a single register screw. After the impression the stuff is passed over a water-roller. Printing on both sides is more particularly employed for the production of curtains and upholstery goods and calico-printing.

CALICO-PRINTING.

The goods intended for calico-printing must be first bleached in the most complete manner possible. Some colours are printed on prepared fabric; others without this preliminary treatment. The preparation consists in padding the fabric in a solution of Turkey-red oil (about 9 oz. per gallon), followed by drying. Some colours, especially alizarine red and rose-red, show up much brighter on prepared stuffs, and this property of Turkey-red oil is also utilised to revivify certain colours that have suffered under treatment subsequent to printing (*e.g.* by chroming), the goods in this case being padded with Turkey-red oil, dried, and gently steamed for a short time.

The different styles of calico-printing are as follows:—

1. Production of the pattern by direct printing.
2. Combined dyeing and printing.
3. Discharge style printing.
4. Reserve style printing.

1. Reproduction of Pattern by Direct Printing.

In this case the principal thing to be considered is the colour, its preparation, and fixing.

The printing colour contains a solution or suspension of one or more dye-stuffs, solvents such as alcohol or organic acids, mordants, tannin, thickening material, and occasionally other substances as well.

The dye-stuffs must be always of the same strength, and consequently have to be first tested by a sample printing. Each dye-stuff is dissolved separately, the solution being used only in a filtered condition. Dye paste should be carefully stirred up before being sampled; and solid dyes must be reduced to the finest possible state of division for use.

The mordants are, for the most part, salts of acetic acid, which are prepared in a concentrated form by the printer, and kept in stock, it being difficult to increase the concentration, though dilution with water can be effected as required. The fixing agent used is tannin, generally dissolved in water and acetic acid.

Oleic acids (Turkey-red oil) are frequently added to brighten colours, but are not used for fixing. Both the mordant and the

fixing agents must be tested by an experimental printing, to determine their quantitative relation to the dye and influence on the shade and brightness.

The adjuncts to printing colours are acetic acid, tartaric acid, sodium chlorate, olive oil, fats (tallow, lard, etc.), turpentine, glycerine, and sal ammoniac; other adjuncts being used only in exceptional cases. Acetic acid serves to dissolve the dye-stuffs and colour lakes, a purpose also served by the less frequently used tartaric acid. Sodium chlorate is added as an oxidising agent to some colours —aniline black, logwood, etc. Olive oil softens the colour and facilitates printing, the same effect being produced by other fats. Turpentine is added to some colours to prevent frothing in the ink-duct.

On account of its non-drying properties, glycerine forms a useful adjunct to many colours, especially such as are prepared with gum or albumin; it prevents frothing, softens the colour, and keeps it from drying on the printing cylinder. Sal-ammoniac, being hygroscopic, is added to colours which it is advisable to prevent drying quickly, *e.g.* aniline black.

Thickening Agents.—These consist chiefly of wheat starch, flour, baked starch, gum, and albumin. Wheat-starch is perhaps the most frequently used for thickening in calico-printing. The paste is prepared by stirring up the starch to a thick pulp, with a little water, and gradually adding more water until a thin milk is produced, whereupon the rest of the water is added all at once, and the whole is boiled until the thickened paste begins to turn a little thinner. It is then cooled and stirred until quite cold, to prevent it getting mouldy.

Boiling is effected in pans of the type shown in Fig. 40. Steam heat is used, the steam being admitted through *f*, *g*, and *h* in the steam jacket *b*, the excess and condensed water being drawn off at *c*. When the boiling is finished, the steam is shut off, *c* is opened, and cold water is run into the jacket from *i*, through *m*. Stirring is effected by so-called planet stirrers *l*, the stirring paddle, in addition to rotating on its own axis, also describing a circular path round the inner wall of the pan. To empty the pan the stirring apparatus is uncoupled at *t*, *v*, and the pan is tipped about on its horizontal axis after the paddles have been taken out. This thickening material is generally prepared in two strengths, the one containing 100 parts, the other 150 parts by weight of starch per 1000 parts of water, the strength being accordingly expressed by $\frac{100}{1000}$ and $\frac{150}{1000}$.

Wheat starch paste is unsuitable for colours containing strong acid or some strong acid salts, which act upon it and convert it

into dextrin, which forms a thinner solution. Acetic acid, however, produces no change, even on boiling.

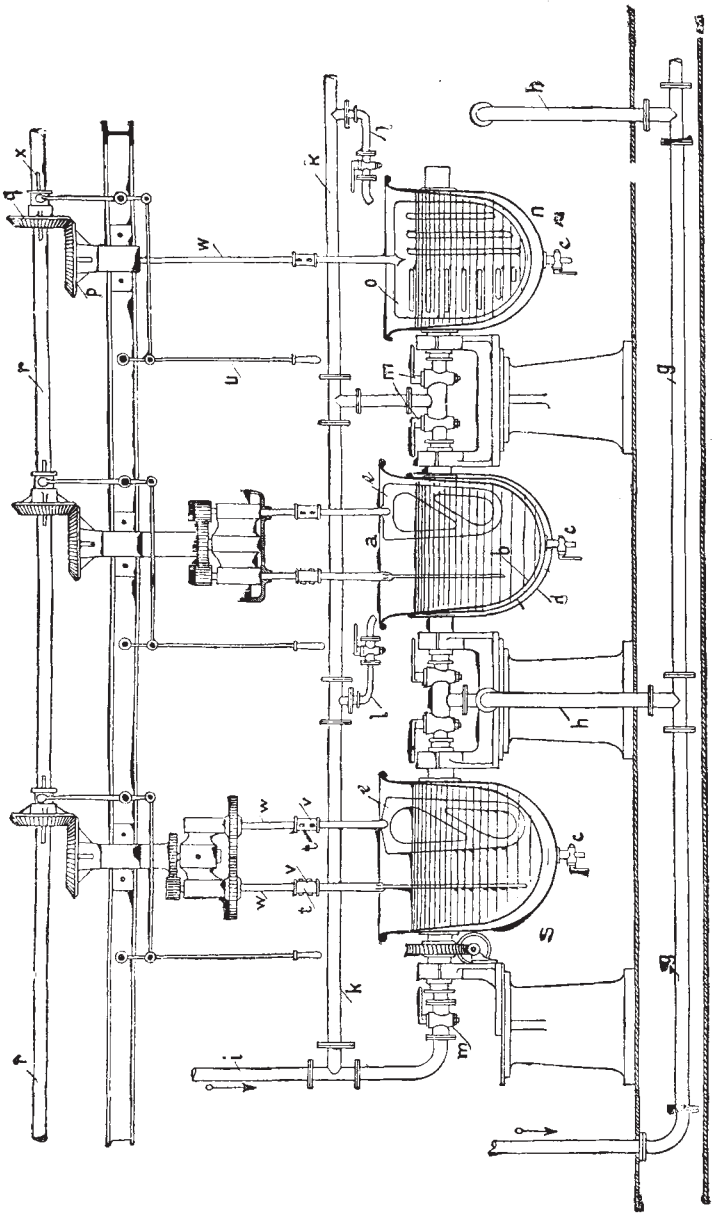

FIG. 40.

As a rule, the starch is merely tested for its thickening properties, and for the presence of insoluble foreign matters such as sand, etc. In the first test, starch of acknowledged quality is

employed for comparison, a thin paste of equal concentration being prepared from each, and their consistence compared by allowing them to drop from a spatula. To test for insoluble matters capable of forming scraper streaks in printing, the starch is stirred up to a thin milk with water, whereupon the solid foreign matter will quickly subside and can be examined after the liquid is poured off.

Two kinds of roasted starch are prepared, namely, light and dark, the former being a light brown powder, which is mixed with water in the proportion of 7 parts to 5, 5 additional parts of water being then added, and the whole boiled for about two hours. To the same class also belong a number of white products, *e. g.* dextrin, prepared by heating wheat starch to about 100° C. with dilute acid; British gum, a dextrin from rice and maize starch; Leio gum is a roasted potato starch, and crommelin and *ly-chow* are similar products. These light roasted starches do not thicken so strongly as starch itself, but are very useful for thin colour. They are soluble in water in all proportions, the thickening solution being prepared by dissolving one part by weight in one to two parts of boiling water.

Dark roasted starch is prepared by roasting starch at about 200° C. In consequence of excessive roasting, it often contains a brown insoluble substance which would choke up the engraving, and must therefore be kept out of the printing colour. To determine the value of starch of this kind, a small quantity, about 10 grms., is dissolved in half a litre of water, and left to stand awhile in a graduated cylinder, the insoluble sediment being then measured. The utility of the sample is in inverse proportion to the amount of this sediment.

This dark roasted starch has only about one-fifth to one-sixth the thickening power of weak starch. In consequence of the sugar content it may serve to retard the oxidation of certain dye-stuffs or iron mordants. When printed it does not penetrate so deep into the fibre as unroasted starch; also when dried it is more readily softened by water, and can therefore be more easily washed out of the fabric than the latter. It is very useful for strongly acid dyes, and is really the only suitable thickening for strongly alkaline dyes. The solution is prepared by stirring up 10 parts of the starch with 5 parts of water, then adding another 5 parts of water, and boiling the whole up for two hours. All the different gums used are chiefly made of gum arabic, tragacanth, and Senegal gum.

Gum arabic is one of the oldest thickenings used, and is particularly suitable for pale clear tints. Both raw and roasted starch cause the fibre to look darker and stronger than when printed with

gum thickening. The colours thickened with gum dry quickly and contract the material, on which account gum is unsuitable for printing mordants, because in this case the colours do not show up full when subsequently dyed.

The contraction of the material by gum can be prevented by adding a little pipeclay. Gum arabic being dear, it is wherever possible replaced by light roasted starch or tragacanth. Frequently it is used for colours that must be applied in concentrated solution, in which case it is strewn in the form of powder. The solution of gum arabic is prepared by stirring up the gum with boiling water, and then either boiling or leaving to stand until dissolved. Should the solution be lumpy, an adulteration with insoluble gums is indicated. The usual strength of the solution is either 1000 parts or 800 parts per 1000 of water. As dissolved gum readily falls a prey to acid fermentation, the solution should be prepared in small quantities only, and stirred in a cool place. Fresh solutions of gum should not be put into vessels containing remnants of old solution.

Senegal gum, although very cheap, is not in much favour; it sticks too fast to the fabric, and therefore can only be used with colours that will stand vigorous washing. It imparts a certain smell to the material.

Tragacanth is a very important thickening, and is used in a thick mucilage or as tragacanth water. The thick mucilage is prepared by suffusing tragacanth with hot water (60 parts per 1000 of water), leaving to stand for twenty-four to twenty-eight hours, and then boiling in a closed cylinder until the mucilage has become perfectly homogeneous (four to six hours). The thickening most frequently employed, especially for tannin colours, is a mixture of equal parts of wheat starch paste and tragacanth mucilage ($\frac{60}{1000}$). This is sometimes known as mark 1/1. The thickening power of all these substances is tested in exactly the same way as with wheat starch; in some cases, especially gum arabic, they are also tested to see if they cloud the thickening colour, for which purpose a sample print is made with a light colour, such as pale blue and methylene blue.

These thickenings are mostly prepared separately, and then added to the corresponding colour solutions and adjuncts before use. A few of the readily soluble substances are sometimes mixed in the solid state with the warm thickening; fats must always be boiled in mixing; dyes and mordants, on the other hand, must only be mixed cold, since otherwise precipitation might occur through the formation of lakes. Formerly the printing colours, especially those containing starch, were generally boiled, *i.e.* the starch was mixed

not only with water, but also with the dye-stuffs and several necessary adjuncts (except mordants), and then boiled for an hour or longer in the same pans as used for making wheat-starch paste (Fig. 40).

Apparently the sole object of this in most cases was to combine the gelatinisation of the starch and the mixing with the other ingredients in one operation. This is still done when a better incorporation of the ingredients can be secured by boiling them all together, *e.g.* in the case of colours containing dye-wood extracts. Since most printing colours contain acetic acid and olive oil, these substances are very often added in preparing the starch paste, from one-tenth to three-tenths of a gallon of 6° B. acetic acid—according to the colour—and about 3½–7 oz. of olive oil per gallon of thickening being used. In the case of starch-tragacanth thickening, the finished tragacanth mucilage is also boiled over again. A special type of thickening is that prepared from albumin, inasmuch as it also acts as a fixing agent on the colour. For bright colours, egg albumin is used; for all others the less pure, but much cheaper, blood albumin. The first named is prepared from white of egg; the blood albumin by freeing blood from fibrin and then evaporating it in vacuum pans. The solution of this albumin in water must be prepared in the cold, about 65 lb. of albumin being steeped in 6½ gals. of water for twenty-four hours, at the end of which time 1½ gal. of turpentine is added to prevent frothing in the ink-duct, and half a gallon of ammonia to keep the solution from turning acid. When the colour, thickened with albumin and printed upon a fabric, is exposed to heat, *e.g.* by steaming, the albumin coagulates, being thereby deposited on the fabric in an insoluble and adherent form, and thus acting as a fixing agent for the colour with which it is mixed. All thickenings must be strained for the removal of lumps and solid particles, and this is effected either by putting them in a bag strainer and forcing them through the meshes of the fabric by pressure and twisting, or placing them on sieves and working them about with brushes by hand or mechanical appliances in imitation of hand labour, in order to rub them through. It is also advisable to strain the finished printing colour after the addition of the thickening material to the other ingredients.

All these thickenings and other dissolved substances used in preparing the printing colour are measured out in graduated copper vessels, which is quicker than weighing; dye-stuffs and dye pastes, however, are weighed. The finished colour is stored in earthenware vessels or wooden casks, which are marked to prevent confusion. If a lighter shade of an already prepared printing colour is required, it may be obtained by diluting the latter with a given weight of the

same thickening that was originally employed; for example, a red printing colour thickened with starch paste and numbered "red 100" is reduced with three parts of the same starch paste; this reduced or diluted colour will then be numbered "red $100\frac{1}{3}$." In diluting tannin colours the diluent thickening should receive an addition of sufficient tannin as to contain approximately the same percentage of tannin as the printing colour itself. This is necessary because the thickening material and the cotton both absorb certain quantities of tannin.

To calculate the cost of a printed article, the amount of colour consumed in printing a single piece must be taken into consideration as well as the price of the printing colour itself. This is done in the following simple manner:—

The colour is weighed before use, and again after a certain number of pieces have been printed, the difference in weight giving the amount consumed.

Employment of Mordant Dye-Stuffs.

Thanks to their fastness, the mordant dyes play a predominant part in calico-printing. They are all so-called "steam" dyes, because the aid of steam is necessary to effect the combination of the dye with the mordant, the formation of the colour lake, and the fixing of the latter on the fibre.

Alizarine is the most important of the series. For red and rose it is used along with alumina mordants (with or without tin mordants); with iron mordants for violet, and with chrome mordants for Bordeaux and brown. In the case of red and rose the goods must always be prepared before printing, as otherwise the colour will come out dull and impure. The blue tinge alizarine marks are used for rose, whilst for red those chiefly consisting of flavopurpurine are taken.

Apart from alizarine red, the following are the principal mordant dyes in use for printing:—Alizarine orange with chrome mordants, for various brown shades; alizarine blue with chrome or zinc mordants, for blue; alizarine Bordeaux with alumina mordants, for amethyst; cœruleine with chrome mordants, for green; gallocyanine with chrome mordants, for violet; logwood with chrome and iron mordants, chiefly for brown and black; quercitron and buckthorn berries with tin, alumina, and chrome mordants, for yellows; catechu with chrome and alumina mordants, for brown; redwood (chiefly on account of its cheapness), for mixed colours.

Other dyes are, of course, used, such as galleine with chrome mordant, for violet; alizarine black with chrome mordant, for grey;

oriole yellow with chrome mordant, for yellow, etc., though not to the same extent; and there are various other dyes suitable for the purposes of the calico printer, the employment of which is kept secret.

Without going into special details, not much can be added to what has already been given as to the preparation of the printing colour. The alizarine dyes are mixed with the thickening, in the cold, whereas dye-wood extracts are generally boiled in the course of preparing the thickening. For producing light shades, the printer usually prepares diluted pastes and extracts from the concentrated commercial articles. The proportions of ingredients taken vary in different establishments; the principal thing is to have the correct ratio of dye-stuff to mordant, and in this respect it is always preferable to have too much mordant than too little, because in the latter case the unfixed dye is loosened from the fibre in the subsequent washing and dirties the material. The mordants used almost exclusively are chromium acetate, chromium bisulphite, aluminium acetate, aluminium sulphocyanide, iron pyrolignite, tin salt, tin acetate, and tin paste.

Employment of Basic Dye-Stuffs.

An important part is also played by the basic dyes in calico-printing, the following being those most in use:—Auramine, brilliant green, malachite green, methyl green, methylene blue, new methylene blue, turquoise blue, printing blue, acetine blue, methyl violet, methylene violet, safranine, fuchsine, and rhodamine. Some of them exhibit a tendency to encrust on the unengraved parts of the printing cylinder, and in such event a bar covered with flannel must be employed at that part of the cylinder where the counter-scraper is usually placed.

The printing colour consists of three portions, all of which are generally prepared separately, *i.e.* the thickening—mostly wheat starch and tragacanth thickening, 1/1 gum water being often used for delicate tints;—a solution of the dye in acetic acid and water, or acetic acid and alcohol; and a solution of tannin in acetic acid and water. For some colours tartaric acid, or ethyl-tartaric acid, is added as well; this last-named acid, acetine, or levulinic acid being employed as a solvent in the case of the indulines. Colourless tannin should be used for bright light tones, especially for light blue. Most of the basic dyes show up better when printed on prepared cloth.

The basic dyes are used in a special manner for the production of the so-called "Lucca" goods, which constitute an imitation of Indian shawls. The goods are prepared by padding with a solution

of sodium stannate thickened with a solution of casein in water and borax. The dyes are mixed with albumin or various metallic salts, such as aluminium acetate and magnesium acetate, with sodium arsenite and aluminium acetate, with arsenicated glycerine, etc., and a thickening material, and fixed by steaming.

All the printing colours prepared with basic dyes are steam colours, steaming being indispensable to fix them on the fibre.

Employment of the Albumin Dye-Stuffs.

Many of the mineral pigments, such as ultramarine, vermilion, chrome yellow, orange chrome, chrome green, various ochres, and lampblack paste (for grey, shaded with ultramarine), being insoluble, cannot be fixed on the fibre in any other way than by mixing them with albumin before printing, the fixation of the colour and the recovery of the albumin being then effected by steaming. Hence these colours also are "steam colours." Occasionally other colours capable of employment in other ways can also be used as albumin colours, *e.g.* buckthorn-berry tin lake, erythrosine—precipitated from its solution by sulphuric acid, and mixed with albumin,—as also solutions of basic dyes, such as methyl violet and fuchsine.

In order to economise the expensive ingredient albumin, it is generally replaced in part with tragacanth mucilage or starch paste; naturally, the lower the proportion of albumin employed, the less satisfactorily will the colour be fixed.

The beauty of the mineral printing colours varies directly with the fineness of division, for which reason it is the general practice to grind the commercial colours (chrome yellow and orange chrome pastes) for a considerable time, in association with a little dissolved gum, in indigo mills. In printing with these colours, the usual inking roller is replaced by a roller brush, and frequently a counter brush must be used as well.

Ultramarine, being difficult to moisten, must be converted into paste with a little alcohol. In using this pigment it must not be forgotten that the same is easily decomposed by acids.

Chrome yellow and orange chrome are printed in association with a salt of cadmium, the object of which adjunct is to counteract the tarnishing effect of sulphuretted hydrogen (PbS) by forming a yellow sulphide.

Several of the albumin colours find their chief use in indigo discharge style printing.

Employment of Direct Dye-Stuffs.

Of these dyes, which play such an important part in cotton-dyeing, only a very small number are used, and that, too, for the

production of light grounds. These comprise chrysamine, chloramine yellow, brilliant geranine, diamine pure blue, etc. For the most part, they are simply mixed with the dressing preparation and applied to the material therewith.

Employment of the Developing Dye-Stuffs.

The method of applying the ice colours is the same as in dyeing, the fabric being prepared with β-naphthol, dried, and printed with the thickened solution of the diazotised amine.

The instability of the diazo solutions makes itself felt here even more than in dyeing. All these colours have the defect of being unable to stand steaming, and being therefore unsuitable for mixing with steam colours. Nevertheless they play a still more important part in calico-printing than in dyeing.

Aniline black, having already been fully described as oxidation black, requires little additional mention here. The same mixture as before is employed, and, being suitably thickened—preferably with dextrin—is printed on the fabric, the black being then developed just as in dyeing. In order to minimise the injurious effect produced by the acid, a portion of the aniline is used in the free state as aniline oil. When the goods are first printed with a lead salt, for the production of chrome colours, the aniline chloride is replaced by aniline nitrate, since otherwise lead chloride would be formed, and would incrust the scraper of the black roller. Also by using the nitrate less aniline is consumed.

Sometimes a so-called aniline steam black is used, the colour being developed by steaming. These colours are either compounded in the same way as Prudhomme black, or else contain yellow lead chromate instead of ferrocyanide. Moreover, in light patterns an ordinary aniline black can be developed by steaming, in which case the printed goods are first developed in the oxidising chamber, then passed through ammonia vapour, and entered in the warmed and closed steamer—on the floor of which one or two pans filled with ammonia have been placed—where they are steamed in the usual way for about a quarter of an hour.

Aniline black always corrodes the scraper to some extent, and this should therefore be ground afresh after a certain number of pieces have been printed.

The history of the evolution of aniline black is very interesting:—

The first aniline black printing colour was prepared by John Lightfoot in 1863, and consisted of aniline, hydrochloric acid, acetic acid, potassium chlorate, cupric chloride, sal-ammoniac, and starch

paste. When this black was printed without copper, by the aid of a wooden roller, it did not develop at all, but the black showed up after being placed in contact with a metal plate for a short time, from which behaviour Lightfoot concluded that metals were essential to the development of the black. However, the employment of soluble copper salts proved a failure, owing to the formation of a precipitate of aniline black within the colour itself. Subsequently attempts were made to obviate this by impregnating the goods with a solution of copper sulphate by padding, and employing a colour, free from copper, for the printing. In this case, however, the white of the fabric must be cleaned by treatment with ammonia. Finally, recourse was had to insoluble copper salts, like copper ferrocyanide or copper hydroxide; in fact, the recommendation made by Lauth in 1864 to use copper sulphide is still followed at the present time. For hand printing, however, copper sulphate must be retained, because the paste preparations readily incrust the block.

It is now known that metals are not essential for the development of aniline black; all they do is to decompose the chlorate, which object can also be effected by the aid of acids.

A further important advance was the introduction of aniline tartrate, as a substitute for the chloride, by C. Koechlin in 1865, thus making it possible to print even the finest fabrics with aniline black without any risk of corrosion. The quantity of tartaric acid employed to dissolve the aniline is between that required for the formation of the neutral salt on the one hand and the acid salt on the other. Without sal-ammoniac it is impossible to obtain a good black; and the action of this salt is explained by the assumption that, by temporarily producing aniline chloride, it helps to start the oxidation.

An aniline black produced with tartaric acid requires much more chlorate—70 per cent. and over—than the ordinary black with aniline chloride. This consideration and the use of tartaric acid render this colour so dear that it is now seldom used.

The mineral colours developed on the fibre in calico-printing are the same as used in ordinary dyeing.

The usual plan in the case of chrome yellow and orange chrome is to print with a suitably thickened mixture of lead acetate and nitrate, and then treat exactly in the manner described in the previous chapter. Iron chamois is seldom used. Berlin-blue is never employed alone in calico-printing, but only as an adjunct to various printing colours, *e.g.* logwood black, and with mordant dyes or tannin dyes for olive green and brown shades, by mixing potassium ferrocyanide therewith, Berlin-blue being then formed, in the presence of acids, by the heat of the steam chamber.

A "steam chrome yellow" and "steam orange chrome" are produced in printing with lead acetate and nitrate in conjunction with barium chromate paste, and then steaming.

A manganese bistre can also be produced as a steam colour by printing a mixture of sodium or potassium bichromate, manganous chloride, and sodium acetate, the oxidation being effected by steam.

Employment of the Vat Dye-Stuffs.

Indigo is fixed on the fibre by the Schlieper and Baum glucose method. Its principal use is in the production of red and blue patterns by over-printing goods dyed with Turkey-red.

The *modus operandi* is as follows:—The fabric is first impregnated with a solution of grape sugar by padding, and then well dried. The printing colour consists of a thickened mixture of finely ground indigo paste and concentrated caustic soda, and the main point to be watched in its preparation is to prevent the mixture heating. The pressure applied in printing should be slight, in order to prevent the colour being forced too deeply into the fabric. The goods are then dried in a hot-air chamber to prevent the conversion of the sodium hydroxide into sodium carbonate—which would have a reducing action in the subsequent operations—and then steamed in a special chamber, where they are exposed for a few seconds to steam that is free from air, the colour being thereby fixed through the reduction of the indigo to indigo white. Next follows, without delay, washing in a copious supply of water, preferably in a roller washer and full width; this removes the caustic soda and oxidises the indigo white to indigo blue.

Other methods for producing indigo blue on the fibre are the "propiolic acid print" and the method with Kalle's "indigo salt," in accordance with which methods indigo should be classed with the developing dye-stuffs.

Indigophenol blue gives fast tones, very similar to indigo, when printed, though unfortunately it is very sensitive to steaming, and therefore cannot be combined with steam colours. Nevertheless a short steaming is indispensable for the fixing of the dye, despite the dulling effect thereby produced; and, indeed, the longer the steaming the faster the colour to washing and soaping.

To prepare the printing colour, the indigophenol is boiled with acetic acid, wheat starch, and tragacanth mucilage, and then mixed cold with a fivefold quantity of 20° B. tin acetate, with which it is left to stand for some time in order to effect the reduction to indigophenol white. After printing, the goods are left in the warm oxidising chamber for about thirty-six hours, then passed

through ammonia vapour, to neutralise the acid in the printing colour, followed by a passage through the Mather and Platt, and by steaming in an enclosed chamber for a half to one hour, under low pressure. A pan filled with ammonia is placed on the floor of the steaming chamber. Finally the goods are washed—also treated with potassium bichromate, if necessary—and hot soaped.

Employment of the Acid Dye-Stuffs.

The acid dye-stuffs which are unsuitable either for the dyeing or printing of cotton, are very seldom used in calico-printing; actually only for the so-called "Lucca" goods. The colours are fixed in the same way as in the case of the basic dyes for the same purpose. The dyes chiefly used are coralline, a few ponceaus, alkali blue, water blue, etc.

Latterly it has been found that the eosines can be fixed on cotton by the aid of chromium acetate, after the manner of the mordant dyes.

For the production of various tints in calico-printing, use is made of the above-named dyes, either separately or in combination.

Green is produced with the green tannin dyes and fast cœruleine, either by itself or shaded with one of the yellows specified, whereby a variety of olive green shades is obtained. Chrome green is chiefly used in indigo discharge style printing.

Bright Yellow.—For this purpose buckthorn berries and tin mordant form the main dye-stuff, auramine and chrome yellow coming next. Various yellows are also furnished by buckthorn berries in association with other mordants, as well as by quercitron, oriole yellow, and light yellow with direct dyes.

For **orange**, use is chiefly made of alizarine orange and orange chrome; for **red**, alizarine and alumina mordant; eventually yellowed and enlivened by the addition of tin mordant; nitraniline red being also used, though this last is unsuitable for combining with steam colours. Vermilion is still largely used in indigo discharge style printing.

Rose-red is produced with alizarine and alumina mordant; for topping, use is made of direct dyes.

Bordeaux is chiefly produced with alizarine and chrome mordant, and with ice colours.

Fast violet tints are produced with alizarine and iron mordant, gallocyanine, and chrome mordant, and a mixture of methylene blue and safranine. Vivid fugitive violets are obtained with methyl violet.

A comparatively large number of dyes are employed for **blue shades**. Pure greenish blue tints are produced with methylene blue, new methylene blue, turquoise blue, and a very greenish ultramarine; for dark blues, use is made of the indulines, or brilliant alizarine cyanines; for grey-blue tints, alizarine blue with chrome or zinc mordants—the colour being more brilliant, but less stable, with the latter; for shades similar to alkali blue, ultramarine and a few direct dyes for topping. Finally, there are indigo blue and dianisidine blue, which cannot well be combined with the steam colours, and are only used for a few special articles.

Dark brown tints are mostly produced with alizarine, logwood, quercitron, and chrome mordants; medium and light browns with catechu—with or without basic dyes and dyewood extracts, or with the last named. In these cases especially an endeavour is made to produce the necessary blue tinge by adding potassium ferrocyanide to the printing colour. Finally, for brown discharge style printings, use is made of manganese bistre, and for single-colour work, the ice colours.

Black is produced with logwood and chrome mordant, shaded with quercitron; indigo bottoming, *noir réduit*, and alizarine black. Grey is obtained with logwood, lampblack paste, or with alizarine black and chrome mordant.

Treatment of the Goods when Printed.

After printing, the goods are passed through a whole series of operations, comprising hanging in the oxidation chamber, putting through the Mather and Platt, steaming, the tartar emetic bath, the chalk bath, chroming, washing and soaping, malting, dung and malt baths, bran bath, chemicking (chloring), and dressing.

Leaving out of the question the last process of all, which will be dealt with separately later on, the object of the series of after-treatments is threefold—(1) fixing the colour; (2) purifying and enlivening the colours; (3) cleansing any white that may be present.

In most cases the goods are not fixed at all in the printing process, and could be completely washed off the fabric; consequently the most important operation of these complementary processes is that of steaming, which effects the fixation of the colour, and, in the case of mordant dyes, develops and fixes the colour lake. The vat dyes and developing dyes alone do not require steaming. The oxidation chamber and Mather and Platt treatments are preparatory to the steaming process, whilst the tartar emetic and chalk baths, and chroming, serve to complete

the fixation of the colour in some cases. All the other operations are performed with the object of removing the thickening materials —since these dull the colours—to cleanse and brighten the colour, and also thoroughly clean the white from any stains arising from the imperfect action of the scraper in the printing press.

The passage through the oxidation chamber and the Mather and Platt are chiefly designed for the elimination of the excess of volatile acids contained in the printing colour. If strongly acid printing colours were immediately exposed to steaming, the liberated acid vapours might injure the colour as well as the goods. Hence it is necessary to pass goods that have, for example, been printed with sulphocyanides (alizarine red with aluminium sulphocyanide) two or three times through the Mather and Platt, or leave them two days in the warm oxidation chamber before steaming. At the same time these two operations also assist in the gradual formation of the colour lake, a consideration not devoid of importance. The goods are hung on rods in the oxidation chamber for about forty-eight hours (the hygrometer registering about 32–36°) during which time they are turned once, so that the parts at the top take up a position at the bottom, and *vice versâ*. Frequently, however, the oxidation chamber is used merely for drying damp goods.

The passage through the Mather and Platt is given for the same purpose, and is employed more particularly when only a short steaming is required. The speed at which the goods are passed through the apparatus is usually regulated so that each portion of the goods makes a sojourn of one minute therein.

Steaming.—The piece to be steamed is backed with a layer of raw cotton, the object of which is to prevent stains arising from drops of condensed water, and is wound upon a collapsible frame, from which it is then removed—by folding the frame—and hung on a rod mounted on a carriage and caused to rotate by means of an attached cog-wheel. A whole series of pieces are hung in this way on the said carriage, which is then run along a track and introduced into the steaming chamber (Fig. 41).

This chamber may be cylindrical or quadrangular, and is fitted at the bottom with steam admission pipes—perforated with orifices directed downwards—and a pipe for drawing off the water, a horizontal partition being provided near the top of the chamber in order to prevent the dripping of condensed moisture. The apparatus must be warmed up before the goods are introduced, since otherwise the excessive condensation of steam might cause the colours to run. With this object the waste pipe is opened to run off the condensed water, after which steam is turned on, and, as soon as all the water is drawn off, the pipe is shut and

the pressure of steam is raised to about half an atmosphere. At the end of about ten minutes the steam and water are allowed to escape, the door is opened, and the goods entered, whereupon the door is shut and steam turned on, without pressure for the first few minutes, after which the effluents are closed and steaming

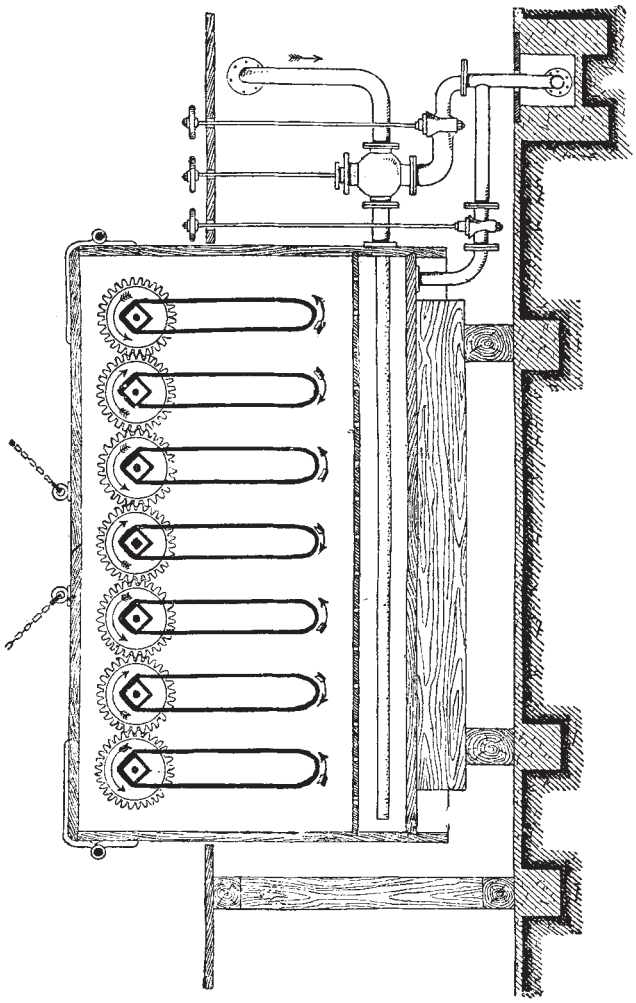

FIG. 41.

continued for a half to two and a half hours, either without pressure or under a pressure of about half an atmosphere, the water of condensation being run off from time to time. Finally, steam is shut off, the doors opened, the carriage drawn out, and another carriage, loaded with goods, introduced in its place, the steaming being then resumed as before. The steamed goods are

unwound, separated from the cotton backing, and passed on for further treatment.

The duration of the steaming process and the pressure employed therein depend on the dye. Albumin dyes are steamed for a half to three-quarters of an hour; tannin dyes for an hour to an hour and a half; mordant dyes for one and a half to two hours. When several different colours are printed on the same piece, the duration of steaming is regulated by the colour that needs to be steamed longest.

Latterly the above method of steaming has been superseded in many establishments by a continuous process, the goods being passed over a series of guide rollers in a chamber filled with steam.

The **tartar emetic bath** is applied only to printings made with tannin dyes, the object being to fix them in a thorough manner by the formation of antimony tannate. The operation is performed in roller becks, through which the goods are passed at such a rate that each part only remains in the vessel one minute. The first bath contains about 3 parts by weight of tartar emetic and 13–15 parts of chalk per 1000 of water, the proportions varying according to the size of the pattern, and, in some cases, amounting to 20 parts and more of tartar emetic. The second bath contains $1\frac{1}{2}$ part of tartar emetic and the same quantity of chalk. The bath temperature is about 70° C. The object of the chalk is to neutralise the potassium bitartrate produced in the bath, the use of other, soluble, alkalis being inadvisable owing to the risk of injuring the colour.

In order to prevent the dulling of delicate colours by the more or less highly coloured bath liquor, the serial order in which the pieces are entered is determined by the sensitivity of the colours; those found by experience to be most liable to contamination by the bath being put through last.

For the same reason the goods are entered face downwards. After the passage of a certain number of pieces, the bath is recuperated by adding more tartar emetic and chalk. Old and foul baths are either run off or else boiled up along with chalk, left to settle, and the clear liquid used over again.

The **chalk bath** is used for goods printed with mordanted colours, and serves to neutralise the residual acid and thus complete the fixation of the colour lake. Just as in the tartar emetic bath, the goods are passed through two roller becks, charged with 1 per cent. of chalk, at a temperature of about 80–90° C., and then through a similar vessel containing clean water. The time of immersion in the bath is about one minute, and the bath is replenished after each piece. Goods that contain tannin dyes in addition to mordant dyes do not require to be put through the

chalk bath, the excess of chalk always present in the tartar emetic bath being sufficient for the purpose.

Chroming is applied to secure better fixation of some colours by oxidation and the formation of a lake. The treatment is applied either cold or hot, and the method of performance varies in different establishments. One point to be borne in mind is that some dyes (*e.g.* alizarine red) may sustain alteration by the partial formation of a chrome lake, and in such case a cold or lukewarm chroming is best. The goods are passed through two roller becks, charged with a 4 per cent. solution of potassium monochromate, though in some instances the first bath alone consists of chromate, the second being merely water, which is frequently renewed. Between the two vats the goods are subjected to moderate pressure by a pair of squeezing rollers. Some articles are treated with chromate in just the same way as in steam chemicking (see later). In chroming goods containing alkaline dyes, the bath receives an addition of a little sal-ammoniac (1–2 parts per mil.), the influence of the alkali on the other colours present being diminished by the formation of ammonia or ammonium carbonate.

The chief purpose of washing is to remove the thickening materials present in the printing colour, and the work is performed in machines of different construction according to the resisting power of the colour. The round washer, similar to that illustrated in Fig. 17, except that the upper roller is here replaced by a folding polygonal reel, is generally used; or the aforesaid vat can be employed, in which case the effect is increased by a beating roller mounted on one side. Goods that are very susceptible to the influence of washing are either left unwashed or washed without rubbing. For this purpose, full-width washing machines have been constructed in which the goods are passed through a series of roller becks fitted in places with a number of beaters; or the goods are made to circulate under water, without rubbing or coming up to the surface. To prevent the goods being dirtied by loosened particles of dye, it has latterly been proposed to add certain metallic oxides (zinc oxide, antimony oxide) to the washing water.

Soaping is chiefly resorted to in order to cleanse the white portions of the goods and to revivify the colours, an addition of a little sodium stannate being often given to the soap bath for this latter purpose, especially in the case of alizarine red.

Marseilles soap is used, and should not contain any free alkali. It is inadvisable to introduce the soap in a solid state into the bath, owing to the risk of spotting the goods by the adherence of soapy particles. A solution of soap is therefore prepared beforehand, and a definite quantity is run into the bath for use, the amount depending

on the number of pieces and nature of the dye to be treated, the usual strength being 3–5 parts of soap per mil. of bath liquor.

Mostly the goods are soaped in band form for about half an hour to an hour, at a temperature of 60–70° C. Soaping considerably increases the brightness of alizarine red and alizarine rose, and in this case the goods are boiled in the soap bath for one to two hours; in fact, occasionally, when heavy patterns of alizarine red are in question, they are soaped twice over, or once under pressure in a copper retort. Tannin colours, not being so resistent, are oftentimes soaped only a quarter to half an hour at medium temperature. Should the goods have a considerable surface of white, it is advisable to soap in a full-width machine.

The **thickening materials may be eliminated** from the printed goods in an innocuous manner by treating them with a decoction of malt, this being especially suitable for starch thickenings on account of the solvent action of malt thereon.

A still better plan is to use a bath of cow-dung and malt, the latter removing the thickening, whilst the decoction of cow-dung cleanses the white with less harm to the colour than by soaping. This method is applied to multi-coloured upholstery goods after a slight soaping, as many as five dunging baths being used. They are charged with 5 parts of cow-dung and 6 parts of malt (both boiled in water) per mil., and used at a temperature of 35° C. After the first two baths the goods are washed.

Some articles—logwood black in particular—are cleansed with bran, by treating them in a hot decoction of this substance once or twice over. The solution is prepared by boiling the bagged bran in water, at the rate of 11–12 parts per mil.

Chemicking, or chloring, serves to bleach the white portions of the fabric that have been left somewhat muddy looking by the washing and soaping processes. It is a very important, and in some cases indispensable, operation, since a perfect white is one of the best qualities of printed goods. There are two methods of application —steaming, and the wet process. In the former case the goods are passed through a trough containing bleaching powder solution, squeezed between rollers, and led into a small wooden steaming chest fitted with guide rollers and a false bottom, under which is a steam-pipe. On issuing from this chest, the goods are washed by a flushing jet and also by passing through a roller beck filled with water.

In the other method the goods are passed, printed side downward, through a pair of rollers, the under one of which is covered with flannel, and revolves in a solution of bleaching powder. They are then led over drying cylinders.

The best strength of bleaching powder solution and the method of application, depend entirely on the resisting power of the dyes. Usually the density of the solution is only a few tenths of a degree B., and it is frequently preferable in the case of very sensitive colours to apply a weak solution twice over than to use a stronger one once.

Frequently the chemicking is combined with blueing, a suffusion of ultramarine being added to the bleach solution, in which event the trough is fitted with a horizontal stirrer in order to prevent the ultramarine from settling to the bottom.

No generally applicable rules can be laid down for these various operations, and experience alone must decide which of them is suited to the needs of any particular case, and how they shall be carried out, in order to produce a beautiful white on the printed goods without injury to the colour. Mordant dyes are treated in the oxidisation chamber—the Mather and Platt—steamed, chalked, washed, soaped, and, if necessary, chemicked. Tannin dyes are put through the Mather and Platt, then steamed, entered in a tartar emetic bath, washed and soaped with care, and finally chemicked (usually by the dry method). Albumin colours are washed with the greatest possible care after steaming; acid dyes, on the other hand, must not be washed at all. For the most part, these printed goods are prepared by the aid of several very different dyes, and in such event the treatment is governed by the most sensitive of these.

Even one and the same article cannot always be treated in exactly the same manner, consequently the progress of each of the prescribed cleansing operations must be watched in every case, and an attempt made to correct any defects by employing some operation not usually practised, or by repeating one or other of the operations already performed.

Some colours that have suffered during the after-treatment can oftentimes be revivified by treatment with Turkey-red oil (see p. 248).

2. Combined Printing and Dyeing.

A second method of producing printed fabrics consists in first printing with one or more mordants and then dyeing with mordant dyes after fixing. Strictly speaking, the articles produced by discharge style or reserve style printing also belong to this category, inasmuch as they too result from a combination of printing and dyeing; nevertheless, the method of working is so different that a separate description is necessary.

The principal consideration in the production of combined effects being the retention of purity in the white portions of the fabric, the operation of oiling previous to dyeing must be omitted, because the oil has a fixing action on many of the dyes.

The suitably thickened mordants must be coloured in order to render the printed impression visible, for which purpose they are mixed with a dye that will easily wash out afterwards, *e.g.* a ponceau. The mixture generally contains an excess of acetic acid. After printing, the mordants are fixed, in the manner described in the section on mordants, and then dyed (*see* Dyeing with Mordant Dyes) along with an addition of size (4 oz. of gelatine per piece of about sixty yards), which prevents the staining of the white. The quantity of dye used depends on the area of the pattern. Red, Bordeaux, violet, brown, and black are chiefly produced in this way.

The mordant used for red consists of aluminium acetate mixed with a little tin salt, yellow-tinge alizarine and size being employed for dyeing out. The stuff is then washed, oiled, steamed, soaped with an addition of sodium stannate, washed, soaped again, washed, and dried in the oxidation chamber. In this case the white must be cleansed by washing and soaping only, since these articles are not chemicked.

Small patterns in alizarine red are also sometimes produced in the same way, notwithstanding the difficulty of cleansing the white. This is done because alizarine red always comes out faster and brighter when dyed than when printed.

The other colours are generally produced in the following manner:—Bordeaux, with aluminium acetate as mordant, and alizarine (bluish tinge), rubine and size as the dye; brown, with aluminium pyrolignite and iron pyrolignite as mordants, followed by dyeing with alizarine and quercitron, under addition of sumach, chalk, and size; violet, with iron pyrolignite as mordant, dyed with alizarine (bluish) and methyl violet, plus size; black, with iron pyrolignite, aluminium pyrolignite and zinc nitrate as mordants, dyed with logwood, quercitron, sumach, and size.

In all these cases, except red, the goods must be chemicked, generally by a double dry chemicking, in order to properly cleanse the white. Black (mourning) goods are mostly treated with bran twice over.

3. Discharge Style Printing.

White or coloured effects may be produced by discharging; in the former case, the task is merely the destruction or solution of the mordant, fixing agent, or the dye itself; in the other, the following

alternative is open:—(1) The discharge is printed along with a dye, towards which it is inert, and which is afterwards fixed on the fabric; (2) a mordant is printed along with the discharge, and the colour is produced by a subsequent dyeing.

Colourless discharges must be tinted before use. Some discharges contain such a large proportion of salts that they must be printed warm in order to prevent crystallisation.

The various methods of discharging may be arranged in three classes—

1. Discharging the mordant.
2. Discharging the tannin-antimony fixing agent.
3. Discharging the dye-stuff.

1. *Discharging the Mordant.*

The unoiled fabric is padded with a solution of alumina or iron mordant and then dried in the cold, to prevent the discharging being impeded by a premature fixing of the mordant.

The discharge is then printed, the goods being afterwards passed once or twice through the Mather and Platt—after a small sample has been dyed out in order to see how the discharge acts—dunged, washed, and dyed. In this process great care is necessary to guard against setting-off on the part of the discharge, and for this reason the goods must not be laid one upon another until thoroughly dry.

The discharge reagents consist of organic acids; and as oxalic and tartaric acid salts are sparingly soluble, ammonium citrate is generally used. The presence, however, of large amounts of free citric acid causes the discharge to run. In discharging alumina-iron mordants or weak iron mordants, an addition of sodium bisulphate is made to the discharge; concentrated iron mordants are discharged with citric acid and tin salt. Latterly, however, the practice of discharging alumina and iron mordants has been abandoned owing to the unreliable character of the operation.

The modern chrome discharge style is produced in a somewhat different manner. The goods are padded with chromium bisulphite, dried, printed with a discharge consisting of sodium chlorate and potassium bromate, steamed for over an hour, chalked, and dyed.

Coloured discharges can be produced on alumina mordants by means of tannin dyes in various ways. For example, the unoiled stuff is first mordanted and fixed, and then printed over with a thickened mixture of a tannin dye, with tannin and ammonium citrate. It is then steamed, entered in a tartar emetic bath, washed, and dyed with alizarine (for red) in association with

Turkey-red oil and size. Only a few basic dyes are, however, suitable for this purpose, *e.g.* thioflavine T, Nile blue, and brilliant green.

2. *Discharging Antimony Tannate.*

The fabric is tannined, fixed with tartar emetic, and then printed with strong caustic soda thickened with roasted starch (containing 50 per cent. of 42° B. soda) and qualified with a little turpentine to prevent frothing. It is next dried, passed twice through the Mather and Platt—which should be charged with dry steam—washed several times, and then dyed with a basic dye, the white being afterwards cleansed by washing, slight soaping, and chemicking.

3. *Discharging the Finished Dye.*

Discharging Vat Blue.—Indigo discharge style is a very important branch of calico-printing, and enables finer details to be produced than is possible by reserve printing.

Three different discharges may be used for vat blue—(1) chromate discharge; (2) chlorate discharge; (3) alkaline discharge.

The chromate discharge is the most important, and the one most in use for colour discharge styles. For the production of a white discharge the fabric is printed with a solution of potassium bichromate thickened with starch — the quantity of bichromate depending on the depth of the blue to be discharged—dried, passed through the discharge bath, and well washed. The discharge bath is used at a temperature of 45–50° C. and contains 4 per cent. of oxalic acid and 5 per cent. of sulphuric acid; the time of exposure is a half to one minute. The bath is contained in a small vat, through which the goods are drawn by the aid of guide rollers. The liquor should be thin in order to thoroughly penetrate the material. After leaving this bath, the fabric is washed under a jet and by passing through a roller beck filled with water.

The part played by oxalic acid in discharging is not yet fully elucidated; it is, however, a fact that sulphuric acid does not act so well in the absence of this acid. The assumption is that an unstable oxide is formed, intermediate in composition between Cr_2O_3 and CrO_3, and parts with oxygen more readily than chromic acid does.

One unavoidable defect of this method is that the fabric is always more or less strongly corroded in the discharged parts. In the case of coloured discharges, however, this defect is absent, since it is unnecessary to discharge the whole of the indigo, and therefore weaker reagents can be used. The colours chiefly employed

are chrome yellow and orange chrome (in paste form), vermilion, chrome green, and various ochres. They are thickened with albumin for printing, this substance then coagulating in the discharge bath and exerting a fixing action on the dyes. In this case neutral potassium chromate must be used as the discharge, since the acid salt coagulates the albumin. Vermilion is the least suitable of all the above-named pigments because of its high price and the readiness with which it rubs off, this tendency varying inversely in proportion to the amount of chromate used for discharging. It is now frequently used in admixture with insoluble red azo dyes.

For pale blue discharge a discharging solution is used that is too weak to entirely decolorise the indigo, but as the resulting colour is too dull to be of any practical value, a little Berlin-blue is added to the discharging agent, or the goods are passed through pure blue. Finally, the colour may be enlivened by the application of a blue dye such as pure blue, methylene blue, etc., in the dressing.

Of late other oxidising agents, such as sodium chlorate and potassium ferricyanide, have come into use, the reaction being aided by steaming. In these cases the material does not suffer corrosion. To produce fast red and blue articles, the fabric is printed with a discharge consisting of sodium bromate, aluminium chlorate, potassium iodide, and copper sulphide; then steamed, and dyed with alizarine. The function of the potassium iodide is stated to be the counteraction of the excess of oxidising agent, which could corrode the fabric (?). The copper sulphide acts as a carrier of oxygen.

Potassium ferricyanide forms an admirable discharge for indigo, in presence of a strong alkali; the method is, however, confined to the production of a bright rose-red with rhodamine, in which case all the other colours that may be present are also produced as alkaline discharge colours. The colours are printed in association with potassium ferricyanide, then dried, and passed through a strong solution of caustic soda.

The discharge of indigo blue with direct dyes has been proposed by the Farbenfabriken Fr. Bayer & Co. The vatted fabric is printed with a suitable dye (chrysophenine, brilliant geranine, etc.), mixed with potassium ferricyanide and magnesium carbonate (as the alkali), and then gently steamed for a quarter of an hour.

The discharge of vat blue with azophore red is proposed by the Hoechst Farbwerke for the production of red and blue articles. The naphtholised vatted goods are printed with a mixture of azophore red, a little caustic soda (to neutralise the acid), and sodium bichromate, and then treated in the usual discharge bath for vat blue.

Turkey-Red Discharge Style.—There are two methods for the discharge of Turkey-red—the "*cuve décolorante*" (decolorising vat), introduced by D. Koechlin, and the caustic soda discharge.

In the first-named and older method, the discharge is effected by hypochlorous acid, the dyed goods being printed with a solution of tartaric acid thickened with dextrin, then dried and passed through a roller beck containing a solution of bleaching powder and quicklime. The lime renders the solution alkaline, and thus nullifies the action of the bleaching powder on the unprinted portions of the goods. The decolorising bath must be tested in advance in order to ascertain whether it has been set in a proper manner for securing the end in view. It should not be too alkaline, or the Berlin-blue here used for the blue discharge will be attacked. On issuing from the bath the goods must be squeezed and at once immersed in water.

For yellow, use is made of a mixture of tartaric acid, citric acid, lead acetate, and a little nitric acid, with which the goods are printed; they are dyed out with lukewarm potassium bichromate after passing through the bleaching powder bath. The lime of the bleaching bath precipitates lead hydroxide on the printed impression, which oxide is converted into chrome yellow in the potassium bichromate treatment. To complete the process, the goods are finally entered in dilute hydrochloric acid and then washed.

For blue, the fabric is printed with a mixture of tartaric acid, oxalic acid, potassium ferrocyanide, and ferrous sulphate. The oxidising action of the bleach bath not only discharges the Turkey-red, but also develops the Berlin-blue.

Green is produced by mixing the discharges for red and blue, and then treating in the same way as for yellow.

At the present time the decolorising method is practically abandoned, the work being of a too delicate character. Difficulties arise in connection with the proper setting of the bleach bath and with the printing of the colours, which are strongly acid and loaded with pipeclay. The printing is performed on the Perrotine press.

In the method now practised, the colour lake is dissolved by printing it over with a highly concentrated solution of caustic soda, followed by steaming. In this case as the ordinary Turkey-red, produced by alizarine, is too difficult to discharge, the goods are mordanted with sodium aluminate and dyed with flavopurpurine and anthrapurpurine. For yellow, the fabric is printed with sodium plumbate, and dyed with potassium chromate. Black is produced with aniline black; blue, with indigo by the Schlieper and Baum method—printing on the goods prepared with grape sugar. The after-treatment is as follows:—The goods are exposed to damp

steam for one to two minutes, then hung for a day in the warm, washed, entered in 6° B. sulphuric acid, washed, dyed with 45° B. potassium monochromate, washed, soaped at 45° C., entered in 2° B. sulphuric acid, washed, passed through a bath of boiling bichromate, and washed again.

The **Chrome Discharge Style** has latterly attained considerable practical importance, but is only applicable to soluble dye-stuffs. The goods are padded, for example, with alizarine blue S and a chrome mordant, dried, printed with the discharge, and steamed. The discharge used consists of potassium ferrocyanide and an alkali, or mixtures of chlorates and bromates, as in the indigo discharge method.

For the illumination of the article, and also for parti-coloured discharges, the direct dyes have been recommended; but only a few of them (*e.g.* chloramine yellow) are able to withstand the discharge reagents employed.

The discharge of tannin dyeings is now a very important process, but is mostly applied to the tannin-antimony fixing agents previously brought on to the fibre, and not to the finished dyeing.

The **finished dyeings** are discharged by printing with strong caustic soda and glucose, or with a mixture of ferrocyanide and chlorates, followed by steaming. Only a few tannin dyeings, however, such as brilliant green, Capri-blue, methyl violet, auramine, pyronine, etc., can be discharged really well.

Discharging Manganese Bistre.—The goods are printed with a discharge consisting of tin salt and citric acid, and then hung cold until the discharge is complete, after which they are passed through a cold chalk bath and washed. For coloured discharges use is made of basic dyes—malachite green and methylene blue,—as well as mineral pigments and colour lakes.

The **discharging of ice colours** in the finished state is a matter of considerable difficulty, and is not even yet successfully accomplished.

Recently a tin discharge, said to give good results, has been introduced for nitraniline red by H. Schmidt.

According to a circular of the Hoechst Farbwerke, the bleach vat is applicable to the discharge of dianisidine blue; but the process is a very difficult one to carry out. The present practice for producing discharge effects with ice colours is to employ the chemical reserves, which will be described a little lower down.

Discharging Direct Dyes.—In this case two discharges are used, one with tin salts, the other with zinc dust. The former are confined to colour discharges, the latter to white.

Not all the direct dyes are suitable for the production of dis-

charge effects, washing fastness being essential as well as sensitivity to discharging reagents. All the dyes that will discharge with tin salts will do so (generally still better) with zinc dust; and the latter will discharge the developing dyes in a satisfactory manner.

The discharge for white is prepared by grinding zinc dust to a very fine state of division, in admixture with a little gum water and glycerine, in the indigo mill. It is then mixed with bisulphite and soda and cooled, thickened in a suitable manner, and printed by the aid of the circular brush. The engraving on the cylinder should be as coarse as possible and shallow, to prevent accumulation of the zinc dust therein.

After the printing, the goods are steamed for one hour under a pressure of half an atmosphere, then passed through cold 2–3° B. sulphuric acid, and finally well washed.

For **coloured discharges**, tin salt (stannous chloride) cannot be used alone, owing to its corrosive action on the fibre; and if neutralised with sodium acetate, does not discharge properly. For this reason a mixture of tin salt, tin acetate, and sodium acetate is employed, or the two first, along with a little citric acid and acetic acid. The dyes used for this style are basic dyes, and are printed on the goods in association with tannin and the discharge. After printing, the fabric is passed once or twice through the Mather and Platt, steamed with dry steam for a half to three-quarters of an hour, entered in a tartar emetic bath, and washed. Most of the basic dyes, however, are partially decomposed into their leuco-compounds by the discharge reagent during the steaming process, and, in order to remedy this, it is then necessary to pass the goods through a lukewarm solution of potassium chromate and dry on a hot drum.

For colour discharges with direct dyes it has been proposed to use certain mordant dyes, such as buckthorn berries, gallocyanine, cœruleine, etc., the dye being printed along with tin acetate and a chrome mordant.

The following direct dyes are very suitable for discharging:— Diamine yellow, benzazurine, heliotrope, Congo-red, etc.

4. Reserve Style Printing.

This term is applied to the process whereby various substances, printed on the fabric, are employed to prevent either the absorption or development of the colours subsequently applied by padding or dyeing. Hence there is no difference in principle between discharging and some reserves which are known as discharge reserves.

The chief reserve style articles are those with vat blue, tannin

dyes, alizarine rose, alizarine violet, ice colours, and aniline black.

Reserve printing under vat blue is perhaps the oldest division of this industry; at present it is mostly produced in the hand-press.

Use is made of a mixture of several substances, the reserving action of which is partly mechanical and partly chemical. The chief mechanical reserves are pipeclay and fatty bodies, which prevent the vat liquor from penetrating the underlying cloth. The chemical reserves consist of copper salts for the most part, these also preventing the fixation of the indigo on the printed places, inasmuch as the indigo blue is oxidised to indigo white if it should penetrate into the reserve coating, and is therefore precipitated in merely a loosely adherent manner on the reserve.

After the reserve has been printed, the fabric is well dried, and is then dyed by short immersions in strong vat liquors, and finally soured and washed without friction. The continuous dyeing process cannot be used, since the friction of the guide rollers would dislodge the reserve. The foregoing method is applied to the production of white reserve patterns. For yellow, the reserve also contains lead acetate, and in this case the goods, after dyeing and souring, are passed through lime-water to neutralise the acid and treated in a warm bath of potassium bichromate at the rate of 11 oz. per piece of about sixty yards, whereby yellow lead chromate is formed on the printed parts. The same method is followed for green, except that the reserve is printed on a slightly blued ground instead of on white, so that the resulting chrome yellow combines with the underlying blue to form green.

Reserve with Tannin Dyes.—The method is performed as follows:—The unoiled stuff is first printed with a reserve containing an antimony salt, and dried; the suitably thickened basic dye and tannin are next applied, well dried (otherwise the reserve will run), steamed under pressure for half an hour, entered in tartar emetic, washed with hot water, and finally soaped lukewarm.

The reserve should contain as much antimony salt as possible; and, as tartar emetic is too sparingly soluble in pure water, it must be mixed with about its own weight of common salt before dissolving. The more readily soluble potassium-antimony oxalate makes a good reserve when thickened with dextrin, without any admixture of common salt.

Reserves under Alizarine Rose and Violet. — For the production of these very handsome and important articles sodium citrate or tartaric acid is printed as a discharge reserve, dried, topped with the dye, and steamed. In the subsequent washing,

the colour lake is thrown off from the reserved parts of the design on which it was unable to fix.

Reserves under Ice Colours.—The processes under this heading have mostly been developed by the Hoechst Farbwerke. Discharge reserves are employed, and are printed on the goods previously prepared with naphthol, then dried, and padded with the corresponding diazo solution on one side. The goods are passed through a pair of squeezing rollers, the lower of which is slightly convex and dips into the slightly thickened diazo solution.

The white reserve style is attended with great difficulties. Nitraniline red is easier to reserve if the Turkey-red oil in the naphthol preparation be replaced with tragacanth, though the red then comes out too dull and yellowish. The best results are obtained with potassium sulphite. For dianisidine blue and the α-naphthylamine dyes a good reserve is formed by a mixture of tin salt and magnesium chloride.

Coloured reserves are prepared with tin salt, tartaric acid, and citric acid, along with basic dyes, chiefly thioflavine, auramine, rhodamine, methyl violet, and brilliant green. The amount of tin salt should be small, to protect the reserve colours as far as possible. The goods, prepared with naphthol, are printed with the discharge reserve, the basic dye and tannin, then dried in the warm oxidation chamber or on hot cylinders (to fix the tannin dye), developed with the diazo solution, washed, and soaped.

For the production of the red and blue article two different methods are employed. According to the process of the Hoechst Farbwerke, the goods, prepared with naphthol, are printed with diazotised dianisidine and ammonium persulphate, dried, passed through diazotised ρ-nitraniline to which a little ammonium oxalate has been added, and finally washed and soaped in presence of ammonium oxalate. The diazotised nitraniline combines with the β-naphthol to form red, except in those places occupied by the dianisidine impression, since the excess of β-naphthol there has been destroyed by the ammonium persulphate. The addition of ammonium oxalate to the diazotised nitraniline is for the purpose of preventing the browning of the nitraniline red by the copper in the dianisidine printing colour.

In the second method for producing the same article (Tschudi & Co.'s patent, transferred to the Farbenfabriken Fr. Bayer & Co.) the procedure is reversed, the goods, prepared with naphthol, being printed with a mixture of diazotised ρ-nitraniline and aluminium sulphate, dried, and passed through diazotised dianisidine; the latter is reserved by the aluminium sulphate, and hence the development of the blue is confined to the unprinted portions of the fabric.

Reserves under Aniline Black.—This article is one of the most important in modern calico-printing. It is produced, by the aid of Prudhomme's black, by first padding the fabric with the solution of aniline ferrocyanide, then drying and printing with a reserve consisting of sodium acetate, soda, and bisulphite, the black being afterwards developed as in ordinary dyeing. The process therefore rests on the circumstance that the aniline ferrocyanide black does not develop until steamed, and that this can be entirely prevented by the aid of alkaline reagents. Sodium aluminate or sulphocyanides can also be employed as reserve.

For the purpose of illumination, use is made of mineral pigments and basic dyes, the direct dyes being less suitable by reason of their inferior brightness. The mineral colours, as well as various colour lakes, are also fixed with albumin. When basic dyes are used, the stuff is padded with a solution of aniline ferrocyanide containing tannin, then dried, and printed with a mixture of dye, tartar emetic, and sodium acetate, the black being developed by steaming.

The newest process for producing the Prudhomme article consists in printing the stuff with a reserve composed mainly of zinc oxide, then drying, and afterwards padding with aniline ferrocyanide solution. Compared with the former method, it offers the advantage of rendering it less necessary to print the goods before oxidation has had time to commence.

5. Topping Printing.

In this method, goods that have already been printed and dried are put through the press again and topped with colour, either all over or in the form of a pattern. In the former event the colours must be in very pale tints, since otherwise the colour of the underlying pattern would undergo a too extensive alteration.

The colours used for complete topping are—alizarine rose, chiefly for the alizarine rose article; alizarine violet, for the corresponding violet article, white reserve being usual in both cases; further, various direct dyes—chloramine yellow, a few diamine yellows, chrysamine, chloramine brown, brilliant geranine, diamine pure blue, diamine violet, etc. For the most part these are applied along with the dressing, and not in the press.

A further application of the same process is when it is desired to dye fabric on the one side only, in which event the stuff is printed with a thickened mordant solution, fixed, and dyed.

The object served by topping a design is either the production of a mixed shade by the superposition of two dyes, or else the discharge of the topping colour on the parts already coloured. In

the latter case the ground colour must contain an addition of a reserve for the topping colour.

Although the method enables the production of some very special effects, it is cumbrous and tedious, especially when several colours have to be applied. The ground and topping colours cannot be applied at the same time, since they would come together in a wet state, and thus produce a mixture of an unanticipated character, or else run. According to Casanova, however, this simplified method of the topping process becomes possible if an addition of turpentine be made to the printing colours.

Wool-Printing.

It is only of late that wool-printing has been practised to any great extent, and it is still far from being as important an industry as that of calico-printing.

The material to be printed must be carefully cleansed. Fine goods and yarns are also first bleached, an operation now performed exclusively with hydrogen peroxide and bisulphite. (*See* Wool-Bleaching).

At an early period it was observed by J. Mercer that in printing half-woollens the dye was very imperfectly taken up by the wool. This he attributed to the reducing action of the wool, probably in consequence of the liberation of the contained sulphur, in the form of sulphuretted hydrogen or sulphurous acid, by steaming. Consequently he recommended that the wool should be prepared by chemicking, a method that is still generally practised.

Most dyes show up much fuller on chemicked wool, though the operation must be performed with great care, or the wool will become yellow and rough. In the case of combed sliver especially, the chemicking must be very slight, since otherwise the spinning and fulling properties of the fibre will be affected. In this case it is better to insufficiently chemick the wool, and to add a little sodium chlorate, as oxidising agent, in preparing the printing colour from dyes that are sensitive to the action of reducing agents, *e.g.* azo dyes. For eosines no chemicking is necessary.

A second method of preparing the wool consists in precipitating stannic acid on the fibre, a treatment that increases the brightness of most printing colours, and also fixes some of them (the eosines, for instance) better.

As in the production of multi-coloured articles the most divergent dye-stuffs are used, it is customary to employ both preparations in the case of finer goods. In such event the goods are damped and padded twice with a $3\frac{1}{2}^{\circ}$ B. solution of sodium stannate, after

which they are left covered up for some time, and then passed through 2° B. sulphuric acid, to fix the tannic acid, followed by immersion in a solution containing 4 per cent. by volume of 3° B. sodium hypochlorite and 0·43 per cent. of 66° B. sulphuric acid (this being less likely to yellow the wool than bleaching powder and hydrochloric acid). The chemicking bath must be kept replenished by a constant influx of a more concentrated solution, since otherwise the first portions of the goods would be more strongly chemicked than the rest.

Hand and cylinder presses are used for printing, as in the case of cottons; common and very wide goods are printed by hand, wool muslins and similar fine goods by the cylinder press. The cylinders must be deeply engraved, and a very elastic pressure secured by the use of thick soft blanket on the backing rollers. The printed goods should be dried very gently.

The dyes used in wool-printing are in general the same as for dyeing this fibre—chiefly acid dyes; and dextrin British gum, and gum, are used for thickening. The printing colours are almost invariably prepared with an addition of an organic acid, chiefly acetic acid, though in some cases tartaric acid or oxalic acid is preferable. For light tints and dyes that equalise with difficulty, it is advisable to employ slightly ammoniacal printing colours. When the colours are required to remain slightly moist after drying, a little glycerine (5–8 oz. per gallon) should be added to the printing colour.

Printing is succeeded by steaming, which fixes the colour. This operation must in this instance be performed damp, since the majority of printing colours on wool do not develop properly under dry steaming; on the other hand, excessive moisture is injurious, since it makes the colours run. Consequently, in order to ensure correct results, the steaming must be effected in presence of a predetermined and readily controllable quantity of moisture, a condition fulfilled by enveloping the goods in cotton cloths previously impregnated with a definite quantity of water (10–20 per cent. of their own weight) by padding or sprinkling. This weight can be ascertained by weighing these backing cloths before and after damping. Steaming is continued for an hour to an hour and a half, according to the dye, and mostly without pressure. A careful washing follows, in order to prevent the soiling of the white by the dye; finally, the stuff is slightly dressed with gum, glycerine, or starch.

Wool-printing is therefore a far easier operation, and one presenting fewer technical difficulties, than calico-printing; in fact, the now so popular discharge printing is the only difficult form.

In this case the chief question is, which of the dyes are suitable for discharging, and which capable of properly resisting the action of the discharge reagents.

As in discharging the direct dyes on cotton, coloured discharges are here effected with tin salt, and white discharges with zinc dust and bisulphite.

Most of the azo dyes discharge well, though here, as in the direct dyes on cotton, there exist difficulties that have not yet been overcome.

The dyes best resisting the discharging action of tin salt, and therefore constituting the most suitable dyes for coloured discharge style, are—the majority of the basic dyes, the eosines, and the acid dyes of the triphenylmethane series.

The colour discharges contain 10–20 per cent. and upwards of tin salt, and about 5 per cent. of sodium acetate. After printing, the goods are steamed for an hour without pressure. The discharge dyes develop best on wool that has been chemicked and prepared with tin. The amount of tin salt depends chiefly on the sensitivity of the dye in question, but also on another circumstance, viz. that in some instances it is not necessary to fully discharge the dye. For example, when a naphthol black dyeing is printed over with a blue discharge containing about 15 per cent. of tin salt, and is afterwards steamed, a sufficiently pure discharge blue is obtained; on the other hand, for an equally good discharge red, 20 per cent. of tin salt is necessary.

For white discharges, the discharge must contain about 40 per cent. of tin salt, and the goods must be damp steamed for ten minutes. However, as it is impossible to produce a pure white in this way, recourse must be had to the second discharge reagent, prepared with zinc dust, bisulphite, and a little soda and glycerine, the reaction being completed by steaming for an hour without pressure.

Silk-Printing.

The same methods and printing colours are used for printing silk as in the case of wool, except that no preparation of the fabric is necessary, and that dry steaming is practised. After steaming, the goods are for the most part only carefully washed, the colours revivified as in dyeing, and given a slight dressing.

In this case also an important part is played by discharge printing with the same discharges; in contrast, however, to wool, a number of effects can be produced on silk by reserve printing (with fatty reserves) and dyeing.

Printing Yarns, Warps, and Combed Sliver.

The printing of yarns is a comparatively young industry, but one that is constantly increasing in importance on account of the possibility of producing a variety of patterns by weaving the partly coloured yarns. Formerly it was the practice to tie the yarn together and dye it at intervals of its length, and subsequently the hand-press was employed for this class of printing; but at present the work is done exclusively on printing frames of special construction.

The printing of combed sliver is termed "Vigoureux printing," and has latterly come very much to the front. The printed sliver is used for the production of mixtures, to which it imparts a very uniform appearance.

The composition and method of fixing the printing colours are, in the main, the same as in cloth-printing.

CHAPTER VI

DRESSING AND FINISHING

THE operations of dressing and finishing comprise all the treatments employed to impart to the fabric the special feel and appearance likely to render it most attractive to the purchaser.

The number of methods employed in the finishing of fabrics is almost beyond count; they may, however, be all classed under two heads—

1. By impregnating the material with various substances;

2. By subjecting it to a small number of mechanical operations, which, however, are performed in very different modifications.

The finishing of fabrics almost entirely belongs to the domain of mechanical technology, its practical performance being only in a very few instances (such as calico-printing) the task of the chemist. Nevertheless a certain degree of acquaintance with this branch of the subject is necessary to the dyer's chemist, on the one hand as supplementing his special knowledge, and, on the other, to enable him to detect many defects that may arise in the course of the various operations coming under the head of the finishing process, which he would otherwise be unable to do.

Finishing may in part precede dyeing, in which event the first part of the process will be the task of the dyer, whereas the remainder is frequently performed in special establishments—"the finisher's."

In the cotton industry the term finishing applies exclusively to the concluding stages of manufacture.

The complete description of this entire process in all its many ramifications can only be given in a work specially devoted to the subject; and the author will therefore confine himself in the following to the means employed in this stage of the manufacture.

The substances used in the finishing process are—

1. Such as are intended to render the material hard and stiff. These comprise chiefly the various starches—wheat, potato, rice, and maize starch; also several starch derivatives, such as dextrin and apparatine; furthermore, gum, tragacanth, size, vegetable mucilage, decoctions of lichens and algæ, etc.

Of these materials the most frequently used are wheat starch, potato starch, and dextrin. The softest dressing is furnished by dextrin, next in order coming potato starch.

Apparatine is a product prepared by treating starch with caustic soda in the cold, the excess of alkali being neutralised with an acid after the reaction has continued for about two hours. Appartine imparts greater stiffness to the material and is less easily washed out than any other dressing.

2. **Fatty substances,** such as tallow, stearin, paraffin, waxes, oils, Turkey-red oil, etc., to render the stuff soft and glossy.

3. **Hygroscopic and softening materials,** to diminish the stiffness of starched goods, such as glycerine, magnesium chloride, zinc salts, ammonia salts, etc. Too much of these adjuncts must not be used, or the cloth will become wet and flaccid on exposure to damp air.

4. **Loading Ingredients.**— China clay (a fine white clay), kaolin, insoluble salts of lime and baryta, etc.

5. **Colouring for the Dressing Preparations.**—Chief of these is ultramarine, which is so largely used in "blueing" cottons and linens, its object being to convert the yellowish tinge of the goods into a more or less pure white. In printed goods the selection of the correct shade of ultramarine is a matter of some moment, since here the degree of whiteness may vary. Some of the ingredients used in the dressing (*e.g.* China clay) absorb ultramarine, the shade of which is then modified accordingly.

Ultramarine is difficult to moisten with water, and should therefore be mixed to a paste with a little alcohol. Dressing preparations containing this colour should not be kept long or they may turn sour, to the detriment of the ultramarine, which is sensitive to acids. To impart a strong blueing to any fabric, it is better to apply a weak ultramarine dressing two or three times over than to treat once with a stronger preparation.

Other colouring matters employed in dressing preparations are Berlin-blue, ochres, direct dyes, basic dyes, etc., either to impart a given shade of colour to a white or printed surface, or else to prevent the colours being dimmed by a superimposed white dressing.

6. **Metals or their sulphides,** in the state of fine powder, for the purpose of producing a metallic lustre. They are prepared by heating the metallic sulphides with fatty substances or by mixing different metal powders, and can be purchased ready for use. They are applied to the fabric by dusting or printing.

7. **Waterproofing** is effected by the application of fatty bodies, caoutchouc solution, salts of alumina or magnesia, etc., either together or separately. The most important process is the water-

proofing of woollen goods, which is generally effected by first impregnating the material with a 2–3° B. solution of aluminium acetate and then passing through steam containing an admixture of fatty substances.

8. **Fireproofing**, or at least non-inflammability, is secured by applying to the stuff a considerable quantity of various salts, such as borax, ammonium phosphate, salts of magnesia, silicates, tungstates, etc. The last-named salts, sodium tungstate in particular, are said to give the best results.

9. **Antiseptics for the Prevention of Mould.**—The majority of the means proposed for this purpose are no use, *e.g.* tannin, camphor, oxalic acid, boric acid, etc.; the most efficacious are zinc chloride, zinc sulphate, and salicylic acid.

The dressing preparations are compounded with the assistance of the ingredients specified above. Sometimes they contain only a single ingredient, *e.g.* a starch, dextrin, gum, size, Turkey-red oil,

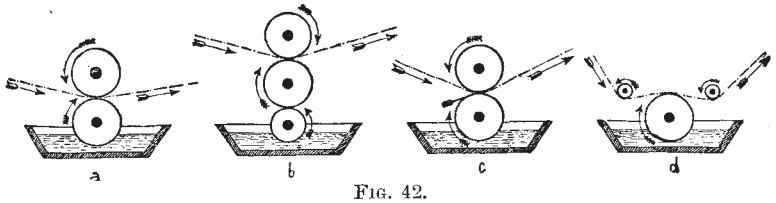

FIG. 42.

etc., applied in the form of a solution or paste; mostly, however, several are employed together, *e.g.* wheat starch and potato starch, or starch and fat, or hygroscopic substances. The number of ingredients may amount to as many as ten, which are mixed together and boiled in the same class of pan as that already described for starch thickening; the product is passed through a strainer.

In most cases the finishing process is not completed by the application of the dressing preparation to the goods, a further mechanical treatment being required to impart the desired feel and appearance to the stuff.

Dressing preparations are confined almost exclusively to cottons and linens, the finishing of woollen and silk goods being usually effected without the aid of these preparations, and merely by mechanical treatment; and even where used at all on these latter goods these dressings are of very simple constitution. Solutions of gum, dextrin, or tragacanth are used for silks, and solutions of gum, size, vegetable mucilage, magnesium chloride, etc., for woollens.

The application of the dressing preparation is in nearly all cases made to the back of the fabric, and is performed in different ways,

according as the quantity used is great or small. This method of working is particularly advantageous in the case of printed goods since otherwise the printed colours would be dimmed by the dressing.

The simplest way is to pass the goods, face upwards, between a pair of rollers, the under one of which is covered with a layer of cotton and dips into a trough containing the dressing preparation (Fig. 42, *a*); the heavier the pressure applied to the rollers the smaller the quantity of dressing that will be left in the fabric, and the farther will it be forced into the material. Another way is to arrange below the pressure rollers a third, which dips into the dressing and distributes it on to the under roller of the pair (*b* in Fig. 42). For conveying still smaller quantities of dressing prepara-

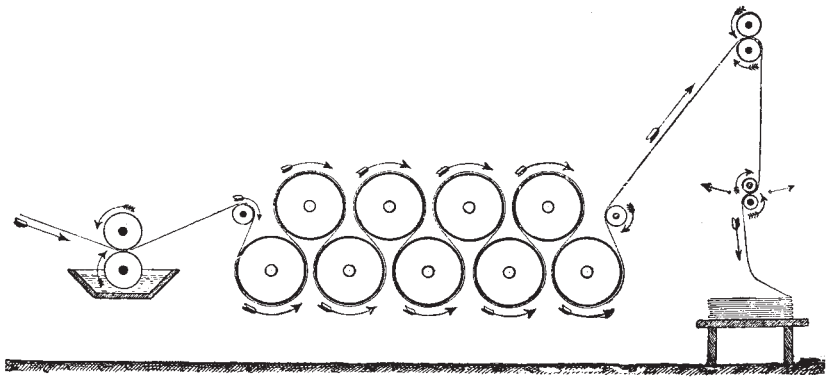

FIG. 43.

tion on to the fabric, use is made of a stippled under roller, fitted with a scraper (*c* in Fig. 42). When the dressing is to be pressed as little as possible into the substance of the fabric, the arrangement shown in *d*, Fig. 42, is employed.

Finally, to apply the dressing equally to both sides, the stuff itself is passed through the preparation and is then squeezed between a pair of rollers.

Where, as in the case of thin preparations containing ultramarine, there is a likelihood of the ingredients becoming separated, a stirring device is provided in the trough; the latter can also be heated in case the application of hot dressings is advisable.

Sometimes, in the case of woollen or silk goods, the dressing is applied with a sponge to the back of the stuff stretched taut in a frame.

After applying the dressing, the next step is to dry it, for which purpose use is made of the cylinder drying machine (in the case of

cottons and linens), *i.e.* a number of heated metal cylinders, generally arranged in two rows, as shown in Fig. 43.

When it is desired that only one side of the material should come into contact with the heated cylinders, these of the lower row are replaced by unheated wooden rollers. This class of drying machine is employed also for drying goods that have not been dressed. In some cases a single large drying cylinder is used, or the goods may be dried on frames (see below) or in the air (silks and woollens).

Frequently the necessity arises for straightening out the goods and stretching them out to their proper width. In such event the drying is effected on the tenting frame, of which there are several modifications. They may, however, all be divided into two main types—the circular frame, consisting of a large drying cylinder, fitted on both sides with adjustable stretchers, and the ordinary horizontal tentering frame, wherein the fabric is conducted over steam plates and hot pipes by means of two hooked endless chains. The stretching device can be adjusted to agree with the desired breadth of the fabric under treatment. There are also stationary tentering frames, in which the cloth is held on the stretch, without motion; these are chiefly used for light cotton fabrics, muslins, tarlatans, etc., and consist of wooden frames, the sides of which are movable, and are provided with clamps for holding the fabric. The latter, when treated with the dressing preparation, is stretched in the frame, which is of the same length as the piece of cloth; it is then stretched to the desired extent, and left to dry in the frame. Similar frames are also used for woollens and silks. Sometimes the sides of the tentering frame are provided with an alternating reciprocal movement, so that the material can be kept moving to and fro whilst drying, in order to distribute the dressing preparation embedded between the individual threads of the fabric, and thus impart a greater uniformity of appearance to the whole.

In finishing cotton goods, the following operations are employed, in addition to those already mentioned:—Damping, gassing, shearing, raising, calendering, mangling, beating, moiréing, stamping, folding, lapping, measuring, and pressing. Of these processes two are employed at a much earlier stage than the rest; gassing before bleaching, and shearing after bleaching is completed.

Shearing is performed in order to remove coarse irregularities, loose ends, naps, etc., and is an indispensable operation in the case of printed fabrics, since these irregularities would spoil the impression, by preventing the access of the colour to the underlying body of the fabric, and thus leaving white marks in the pattern on

the subsequent removal of the loose ends and naps. Various forms of shearing machine are employed, the cutting being usually effected by a revolving cylinder, carrying a number of spiral steel blades, working against a fixed horizontal knife. The fabric is first passed over brushes which raise up the loose ends, fibres, etc., into position for removal by the cutting mechanism. Usually these machines are fitted with two sets of cutters and several brushes, to enable the stuff to be shorn on both sides.

After leaving the shearing machine, the pieces are opened and brushed, to remove the cut fly, and are then finished—if to be left white—or dyed, printed, etc.

Damping follows starching and drying, in order to fit the goods for the subsequent treatment, the fibres lacking the requisite flexibility when dry. The damping machine employed for this purpose consists chiefly of a quick-running brush, partly immersed in a trough of water, which is thus discharged, in the form of a fine spray, on to the goods as they are drawn by. A screen of fine gauze is interposed between the brush and the goods in order to keep back large drops of water, which would otherwise render the damping irregular.

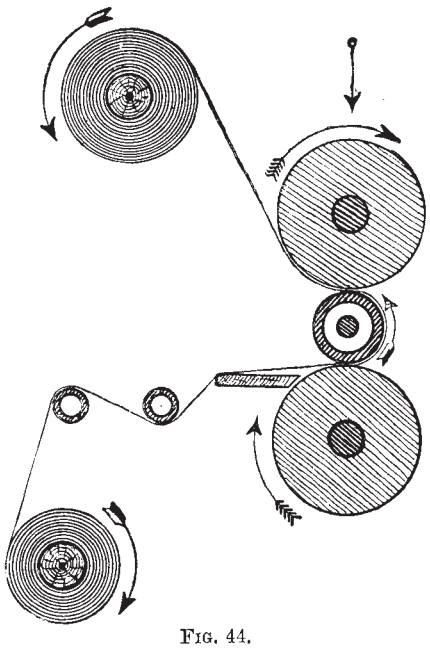

FIG. 44.

Goods intended for stiff finish are not put through any further finishing process, properly so called; but those required to exhibit softness and lustre are next calendered. The calendering machines used, for the most part, consist of three superimposed rollers, subjected to heavy pressure, the middle roller being of steel, the other two being made of paper (Fig. 44), by pressing a number of layers of very good class paper upon steel cores. The use of steel rollers throughout would be calculated to damage the fibre under the heavy pressures employed. According to the effect desired, the goods in the calender may be fed either between two of the cylinders or all three. This treatment breaks up the cohesion of the dressing preparation, and imparts softness and gloss to the fabric. Hot

calendering gives a better gloss, and therefore the steel cylinder is provided with a steam-heating arrangement. To obtain the highest degree of gloss, the goods are put through the friction calender, which has two steel cylinders and an intermediate paper one, the friction being produced by running one of the steel cylinders faster than the other. The effect is sometimes heightened by giving the steel cylinder a lateral motion as well. If a single passage through the machine does not produce the desired result the operation is repeated. Calendering machines are now made with a larger number of rollers (up to six).

The action of the calender greatly depends on the nature of the dressing preparation employed. Thus, if the fabric be dressed merely with wheat starch, it cannot be raised to any special degree

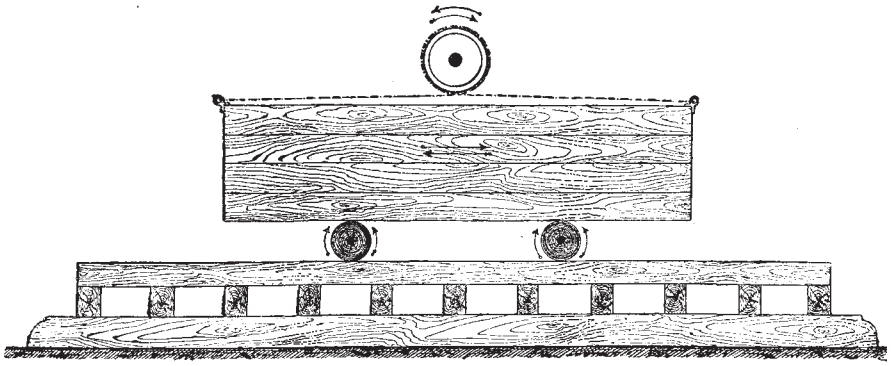

FIG. 45.

of softness and gloss by repeated calendering, the operation being therefore restricted to crushing the dressing. For glossy finish, use is made of fats, waxes, stearin, etc.

Sometimes unstarched goods are calendered, the object being to make them denser in texture, in order to retard the penetration of the printing colour or the subsequently applied dressing preparation.

A process similar to calendering is that of mangling. Box-mangles are generally used, consisting of rectangular wooden boxes (Fig. 45) filled with stones and lumps of old iron, and run to and fro over a couple of rollers, on which the fabric to be mangled is wound tightly and without creasing. The goods must be damped in a perfectly uniform manner, since otherwise the fabric might become weakened under the enormous pressure applied. According to the finish in view, the rollers are large or small, and made of wood or metal,—large wooden rollers furnishing the best gloss of all. As a rule, the goods are left in the mangle during four to six double traverses of the weighted box.

Beetling is a stamping process which produces an atlas-like gloss. The goods are wound on a wooden roller, covered with calico and situated underneath a row of wooden stamps actuated by lifting cams (Fig. 46). There are usually two pieces in a length, and three lengths side by side on each roller.

In the section shown in the drawing, the lifting cams are represented by *b*, and are mounted, spirally, on the shaft *a*; *c* is one of the wooden stamps; *e* is the full roller in the machine; *d*, one that is finished, and *f*, one filled with cloth ready for insertion in the machine.

The rollers revolve at slow speed, and at the same time are

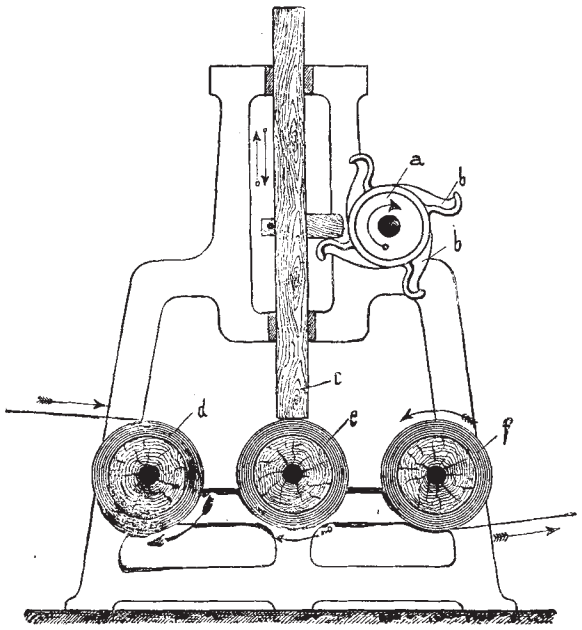

FIG. 46.

moved to and fro longitudinally. After being beetled for about half an hour, the goods are taken out, wound on another similar roller, and put through the same treatment over again.

In the new Mather and Platt beetles, the wooden stamps are fastened to metallic springs and are much more productive than the older form. They have not yet, however, been able to entirely displace the older machines, the latter furnishing better results in point of quality.

Some fabrics are moiréd or stamped.

Moiré or watered effects are optical effects produced by compressing some parts of the threads flat, and leaving the remainder

in their natural condition, thus producing the impression of a pattern.

Various methods are employed for this purpose—

1. By running the fabric double through the calender;
2. By mangling;
3. By calendering between two rollers, one of which is smooth, the other engraved with a large number of mutually intersecting lines; a lateral movement is also imparted during the rotation;
4. The fabric is subjected to the action of an engraved roller bearing a moiré design.

Soft fabrics alone are suitable for this process, and consequently fatty dressing preparations are employed.

Stamping consists in producing a raised design by the aid of an engraved roller, and can therefore only be practised on soft finish goods. A three-cylinder calender is employed, the middle one being of metal and engraved, the two others of paper.

Some goods finished with fatty dressings are also lustred or glossed by ironing with a steel iron.

The final operations in finishing cotton goods consist of folding, lapping, measuring, and pressing, each effected by the aid of special appliances. Pressing, the object of which is to reduce bulk, is mostly performed in hydraulic presses where a large number of pieces, arranged side by side and piled one row on another, and separated by plates of zinc or boards, are treated at one operation.

The selection and performance of the foregoing operations in the finishing process depend on the quality of the goods, and may differ considerably. Some white goods are not dressed at all, but are simply damped and calendered hot (so-called "natural finish"). Hard finish is produced by merely starching and drying, and "half smooth" finish by a second calendering, etc.

Raised goods (flannels, fustian, calmuck, etc.) require a special treatment to produce a soft nap or pile on one or both sides of the stuff. This is effected in the raising machine, which mainly consists of horizontal cylinders arranged in a semicircle and fitted with a number of steel points. One part of the set is moved in one direction, the rest in the opposite direction. The goods to be raised must be perfectly dry. Raising is applied to both white and coloured or printed goods; in the latter cases the raising may be effected before or after dyeing or printing.

Raised cotton goods of this kind serve as cheap imitations of woollen goods.

Linens are finished in just the same manner as cottons. In this class of goods the beetling process plays a very important part,

and imparts to these fabrics their highly prized gloss. Linens are not put through the raising process.

Hemp and jute goods are generally calendered under heavy pressure, in order to press the threads out flat, and thus give the fabric a closer appearance.

The finishing of silk goods resembles that of cottons, inasmuch as the same operations, or nearly so, are employed in both cases. However, as stated in the introduction, silken fabrics are rarely stiffened with dressing preparations; and these, when used at all, are of very simple constitution, containing nothing but gum, dextrin, or size.

Each separate quality and kind of fabric requires special treatment. As a rule, the fabric, on leaving the loom, is cleaned by means of steel roller brushes, then shorn or gassed, rubbed with smoothly polished steel plates to straighten out the threads, and eventually coated, while in a stretched condition, with dressing preparation, applied on the back; then dried and pressed or calendered. Properly woven silk goods are mostly only warm pressed after the projecting fibres have been removed and the threads straightened out and stopped. The pressing is effected either in the press, with hot plates, or in the calender. The finest silks are merely smoothened by cold pressing. These fabrics are neither raised, beetled, nor mangled.

Finishing Woollens.—Woollen fabrics are put through a more complex finishing process than any other kind of textile goods. The methods employed depend on whether the fabric belongs to the woollen or the worsted class. In either case a large number of operations have to be gone through, according to the quality, etc., and these consist of various mechanical treatments, the application of dressing preparations being seldom resorted to.

Of the operations already described, those of beetling, mangling, moiréing, and relief-stamping are never applied to woollens; and the other processes of tenting, shearing, raising, and pressing are performed in a different manner from that practised in the case of cottons.

Shearing is effected in special shearing machines. Raising is an important operation, especially in the case of woollen cloths, and is performed with card clothing nailed on wooden rollers, a series of these rollers, arranged in a semicircle, forming the principal feature of the raising machine. Dull carding pins are employed in the first stage, in order to bring up the nap slowly, with a minimum of injury to the felt, and develop the pile in a gradual manner. Subsequently sharper pins are used to stroke out the

pile, smoothly and in one direction, on the surface of the cloth.

The fabric must be raised in a damp state, since when dry the fibres are not sufficiently supple, and are liable to injury during the process. On the other hand, the fabric must not be too wet, or the carding pins will become too soft. The longer the cloth is raised in a semi-wet state, the better the gloss and the more firmly will the nap be stroked down on the surface.

Pressing is a far more important operation in the finishing of woollen goods than in any other fabrics, and is performed in a special manner for each different class of material. Hot pressing alone is given, since it is only by heat (or moisture) that the wool hairs are rendered flexible. Hydraulic presses are generally used, the goods being piled up, a number of pieces together, with hot metal sheets between each two pieces, and layers of millboard between the separate folds of the cloth. The modifications of this operation consist in differences of duration and degree of pressure applied, the greatest lustre being obtained by prolonged exposure to heavy pressure. To produce high lustre the cloth is pressed several times under heavy pressure and for some hours at a time, being often left in the press all night. The pressure is applied lightly at first and increased afterwards. Some woollens are pressed for only a few minutes, the object in such cases being merely to smooth them out without producing any lustre.

A variety of continuous pressing, usually employed as a preparation for the actual process, is effected on the trough press, a machine consisting of a trough-shaped metal plate in which a metal cylinder slowly revolves, both being heated. The fabric passes slowly between the cylinder and the plate, and is thereby gently pressed and smoothed.

The finishing of woollens also comprises three operations that are unknown in the finishing of other fabrics, viz. steaming, crabbing, and fulling or milling.

The steaming process is also known as "decatiring," from an old French word meaning to deprive of lustre, though, as a matter of fact, this sense of the word is only applicable to one modification of the process, namely, the removal of the greasy lustre produced on woollen cloth by pressing, the pile of the cloth being caused to stand up a little by passing the fabric over an arched plate of perforated metal through which a current of steam is being passed.

In the process of steaming, properly so-called, the fabric is wound tightly around a perforated metal cylinder, through the axis of which steam is admitted to the interior. The steam renders the pile soft and plastic, and fixes it in the position it has been caused

to assume by the mutual pressure of the superimposed layers of cloth. The more tightly the stuff has been wound on the cylinder and the longer it is steamed, the greater the resulting lustre.

Some articles are steamed for a long time, and then left to cool down before being unrolled from the cylinder; others, again, are steamed for only a few minutes, and immediately unwound; from which it is evident that, like pressing, this operation can be performed in a variety of ways.

In other cases, again, the goods on the steaming cylinder are immersed in a vat or chest into which steam is admitted, *i.e.* steam is applied to both sides of the goods at once.

Crabbing is a mild form of steaming applied chiefly to half-wool goods. In this operation the goods are more or less tightly wound on a roller, which revolves in a vessel of hot water. This treatment softens the pile and fixes it in its existing position, with the result that the subsequent displacement likely to occur, owing to different degrees of hygroscopicity in the fibres of these mixed fabrics, is retarded.

Fulling or milling is principally employed in the production of woollen cloth, and is an operation based on the felting capacity of wool fibre. In performing this treatment, the woollen fabric is fastened end for end like a sack, and impregnated with a solution of soap in a fulling mill (see Fig. 47), where it is left for some considerable time.

The fulling mill consists chiefly of two adjustable rollers, a_1, a_2, through which the material is passed in its full breadth; c_1, c_2, are the real milling rollers; d is a conduit in which the goods are pressed into folds; e is the flap closing the outlet of same, and f the spring acting on this flap.

Fig. 47 also shows the feed conduit, b; the band of cloth, g; a perforated board, h, which tips up when a knot occurs in the band, and thus stops the machine; i is a flap through which the fulling liquor is introduced, and k is the door.

The effect of the milling process is in direct relation to the length of exposure, and also depends on the setting of the aforesaid rollers. Thus, for example, a piece of cloth 50 yards long can be milled until the length has shrunk to 30 yards; again, military blankets can be shrunk from their original dimensions of $11\frac{1}{2}$ ft. by 82 ft. to 5 ft. by 65 ft. in about four hours.

Slight milling is also applied to some worsted fabrics, and even to mixed fabrics, special effects being often produced by this means.

The process known as "impregnation" is often combined with milling, and consists of incorporating shorn hairs with the fabric

by adding to the latter in the fulling mill as much as 20–25 per cent., and sometimes up to 70–80 per cent., of its own weight of the pile hairs obtained by shearing the cloth. These are applied to the underside of the material, with which they become incorporated, thanks to the felting property of the fibres.

Much has been written and discussed of late respecting the acid process of milling, wherein the soap solution is replaced by sulphuric acid. Up to the present, however, the method has only given good results in the manufacture of felt.

Finally, a process of curling is employed, chiefly for the purpose of imparting a curly appearance to the surface of winter

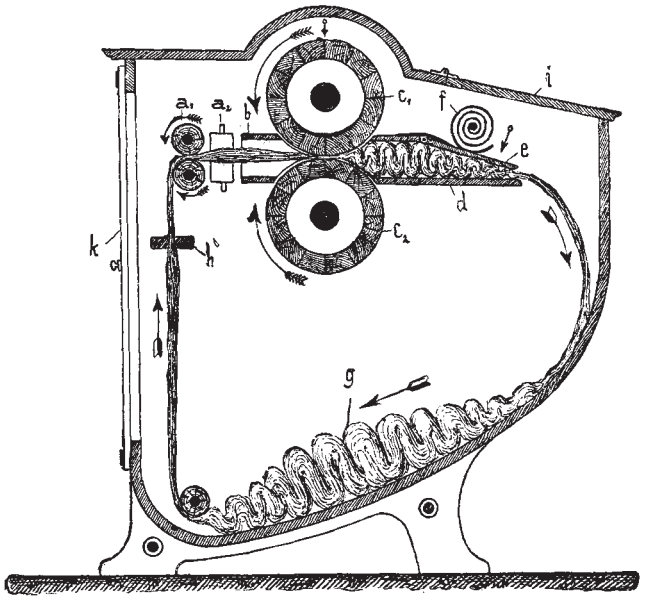

FIG. 47.

overcoatings. In this process a plate, fitted with a brush, is pressed on the damped cloth, and set in motion in various ways, mostly rotatory, the motion influencing the style of curl produced.

The complex character of the finishing process applied to woollen fabrics may be gathered from the following summary of the operations comprised in two very common modes of finishing:—

1. A smooth, so-called "Oriental" cloth, on issuing from the loom, is first washed with soda, then milled, carbonised, raised twice, tented, shorn, passed through the trough press, pressed in the hydraulic press, and steamed. Up to this point it is immaterial whether the stuff has been dyed in the wool or will be in the piece but from this stage onward their treatment is different, piece-dyed

goods being then dyed, washed, dried on the tenting frame, shorn, and (generally) pressed thrice. Wool-dyed goods are damped, raised, shorn, pressed, steamed, and pressed twice.

2. Worsteds are mostly nepped, washed with soap and soda, dried, gassed, brushed, gassed, damped, steamed, tented, dyed, washed, crabbed, tented, shorn, pressed, steamed, and pressed again.

THE END

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