

Dyeing may be generally divided into two portions, direct and indirect, which will be studied and discussed in the subsequent paragraphs.

DIRECT DYEING.

Direct dyes (substantive dyes) are those where the coloring matters brought in contact with silk combine with it or become fixed without the aid of any intermediary agent.

Direct dyes may be subdivided into three classes:

1st. Those where the color is developed upon the fiber. Indigo, as applied in the vat, is the only type of this class.

2d. Those where the coloring matter is absorbed by the silk, but without true combination.

3d. Those where the coloring matters are fixed profoundly upon the silk, or rather combine with it so intimately that both reciprocally lose their characteristic properties.

In the first class, that of the blue vat, the fiber of the silk is saturated with an alkaline colorless solution of indigo, which, on aeration is converted, on the fiber itself, from soluble indigo-white to insoluble indigo-blue, the precipitation taking place in the silk.

In the second class the silk fiber behaves with coloring matters just as wood-charcoal and bone-black behave with certain gases and dissolved substances.

The coloring matters are then fixed by the porosity of the silk, but neither undergoes any modification. There is no true combination, and in several cases, as in that of extract of indigo, it is easy to strip the shade and to restore the silk to its original condition.

Thus, if a color like extract of indigo has been applied alone or slightly acidulated, it may be removed from the fiber by simple treatment with a lukewarm alkaline bath, just as might be done with wood-charcoal or bone-black.

The third case comprises substances which have, in the proper sense of the word, an affinity for silk, and to this class belong especially the astringent matters of tannins. These substances possess a great affinity for proteic matters, with which they combine in enormous proportions, whilst in the second case only small quantities are concerned.

Both the silk and the astringent principle lose their properties in part, and it is impossible to restore them completely.

INDIRECT DYEING.

Indirect dyes (adjective colors) are those which require an intermediate agent or mordant to aid in the fixation of the coloring matter upon the fiber. Such dyes are generally applied in two operations, the first consisting in fixing the mordant, and the second in depositing the color upon it.

Indirect dyes are subdivided into two classes:

1st. Indirect dyes properly so called.

2d. Dyes depending on the formation of an insoluble metallic precipitate upon the silk, in a greater or lesser quantity.

To the former class belong the bulk of the old dyes with woods, roots, etc. Silk, for instance, dyed directly in a solution of logwood, would take a mere dull fawn-colored stain; but if previously mordanted with iron, copper, or alumina it will take, according to the mordant, black, blue, or violet shades, true precipitates which are formed upon the fiber, and which agree in color with the precipitates (lakes) formed by mixing the same materials in test glasses. Such dyes are generally fast as against alkaline reagents which usually strip direct dyes. With acid reagents the reverse is the case. In general acids aid direct dyes, and reduce indirect dyes by laying hold of the metallic oxides which have been fixed.

In indirect dyeing with mordants the attention of the dyer must be turned towards depositing them perfectly level, otherwise when the dye comes to be applied the consequences will be disastrous.

The mode of action of the mordants, which are always metallic, will be seen in the following paragraph. There is, nevertheless, one case where the mordant is organic, formed of tannins, as occurs in dyeing black.

Indirect dyes, which depend on the formation of a metallic precipitate, play but a small part in silk dyeing. The precipitates formed upon silk by the fixation of a first salt, such as a salt of iron or of lead, followed up under suitable conditions by the action of a second salt, such as yellow prussiate, bichromate of potash, etc., in order to form blues or greens, affect its luster and its softness too much; so that these methods, employed for cotton, are abandoned or nearly so as regards silks.

Silks, therefore, to sum up, are dyed directly or indirectly.

Directly: either by fixation of a soluble color which becomes insoluble through oxidation or exposure to the air, as in the blue vat;

Or by a simple action of porosity akin to the decolorizing power of bone-black. Examples are the artificial colors—indigo-carmin, etc.—in general; in this case acids facilitate the fixation of the color, and alkalis tend to loosen or strip it. There are a few exceptions to this rule, such as orchil and annatto, which work on in an alkaline solution;

Or by chemical affinity, properly so called, to which class belong the astringents; and the properties both of these bodies and of the silk are modified by an act of true chemical combination.

If silks are dyed with certain coloring matters by the aid of an indispensable intermediate, the dyeing is indirect, and the intermediate takes the name of a mordant, and consists in a metallic oxide. The shades with one and the same coloring matter vary according to the oxide, and as a rule such colors support alkalis but not acids.

Indirect dyes may occur in several distinct cases.

Either they are produced by the action of the coloring matter upon an oxide fixed as a mordant, the most common case;

Or by the fixation of a metallic precipitant upon a metallic compound previously fixed;

Or by the fixation of a metallic precipitate upon a body of the astringent class, such as catechu or galls deposited upon the silk.

Mordants, which have been in use for a long time, still constitute one of the bases of dyeing, despite the invasion of the modern artificial colors. The latter, indeed, give all the colors of the rainbow without, like the wood colors, undergoing changes under the influence of metallic salts, and have almost expelled them from the department of clear, bright colors; but it is not the same with saddened colors and blacks, which are generally produced by the use of several of the wood colors modified by the action of the mordants.

The commonest mordants are those of alumina, tin, iron, and copper; then follow those of chrome, manganese, mercury, etc., less used in silk dyeing.

ALUMINA MORDANTS.

To fix alumina upon silk the only agent formerly known was alum.

At present, besides the different qualities of alum, the dyer has at his disposal other aluminous mordants, such as sulphate of alumina, hyposulphite of alumina, acetate of alumina, aluminate of soda, and, quite recently, a solution of alumina in methylamine has been proposed. If this last can be produced at a low price, it will be the most active aluminous mordant.

Alum is the salt most commonly used, and it occurs in three sorts:

Roman alum.

Alum in the Roman style.

Ammonia alum.

The two former are potash and alumina alums, of the formula $KO, SO_3 + Al_2O_3, 3 SO_3 + 24 HO$.

Roman alum, the kind most anciently known, is prepared from a mineral named alunite, and is now rare and much sought after. It has a rusty tint, formed by a deposit of (insoluble) peroxide of iron. This rusty tint forms, moreover, in consequence of the manner of manufacture, layers alternating with other layers perfectly white.

Later, when alum, identical with that of Rome, was made in France and elsewhere, in order to find a market for it, it was necessary to give it this rusty tint by means of some red ochre.

Roman alum is valuable on account of its great purity, especially its freedom from iron, which is a very pernicious ingredient; for if alumina tends to give bright colors, iron, even in very trifling proportions, tends to sadden. An alum intended for delicate colors ought to show no immediate blue coloration or precipitate if tested with prussiate of potash. As to the rusty tint which characterizes Roman alum, although due to iron, it is entirely without action upon the coloring matters. Being perfectly insoluble in the dye bath, it settles to the bottom like so much sand.

In our days ammonia alum, on account of its low price, is substituted for Roman alum. The first and commonest kind is somewhat iron, but may serve for blacks (?) and saddened shades. The second kind, refined alum, is obtained by recrystallization of the former. It is less ferruginous and higher in price.

Finally, the third kind, or so called double refined alum, is obtained by a further recrystallization of the former. It is pure enough for the most delicate shades and may rival Roman alum.

[We must here remark that ammonia alums are becoming scarcer, and potash alums are regaining something of their old supremacy.]

The process of aluming silks may precede all the dyeing, or it may take place in the course of the operations. In the former case the alum bath may be permanent, while in the latter it is generally run off after using.

To alum silks they receive three or four turns, and are then put to steep at the bottom of the alum beck, where they are left for several hours, ordinarily over night. The solution of alum should be saturated in the cold, and should be refreshed from time to time with a boiling and concentrated solution of alum. The same end may be gained by keeping in the beck, just beneath the surface of the liquid, a bag full of fragments of alum, taking care to stir up the bag well before the introduction of each lot of silk.

For aluming, the silk ought always to be suitably moistened, the skeins containing about their own weight of water. If the silks were introduced dry, they would dye badly, and in some cases they would not very easily become wetted by the dye bath. A consequence of this indispensable degree of humidity is, that permanent baths are gradually weakened and require an addition of coloring matter, etc., if they are to be maintained at one constant strength.

Alum is applied in the cold. When the silks are taken out, they must not be dried off from the alum, as they would otherwise take a bad feel, and could not be moistened without difficulty. On the contrary, when well drained, they are rinsed moderately in running water.

In aluming very little alum is fixed upon the silk, and the small quantity that is thrown down depends on the rinsing, which is preferably done in calcareous water. In this case the bicarbonate of lime contributes to the precipitation of alumina upon the fiber.

The aluming of silks which have already undergone certain dyeing operations is conducted substantially in the same manner, but the bath may be slightly heated, and is generally thrown away after use.

Sulphate of alumina, which now plays a certain part in wool dyeing, has not hitherto proved very successful for silks.

The most active preparation of alumina, which may, perhaps, be called the mordant of the future, is a solution of gelatinous alumina in methylamine. This compound, which may be regarded as the aluminate of methylamine, if exposed to the air, loses its methylamine, which is very volatile, while an abundant deposit of alumina is left without fear of injuring the fiber.

Alum ought to be as neutral as possible; it yields, then, with decoction of logwood, a very intense reddish violet, while if the alum is acid the color turns to a yellowish brown.

M. W. Stein recommends the use of ultramarine as a test, as its color is destroyed by the least traces of sulphuric acid in the alum.

[It must be remembered, however, that different makes of ultramarine have different powers of resisting acids.]

If the dyer uses sulphate of alumina, a salt usually acid, he may easily take account of this excess of acid by washing about 75 grains of the sample, pulverized in absolute alcohol, which seizes the acid, and leaves the pure sulphate, which is almost insoluble in alcohol. It is then easy to determine the quantity of free acid in the alcohol by diluting it with water and submitting it to an ordinary acidimetric operation.

[If any of our friends are disposed to make use of this test, we should advise them to dry the samples of sulphate of alumina first at a heat not exceeding 212° Fahr. Otherwise, in case of damp samples, the alcohol would be considerably diluted by the water present.]—*Chemical Review*.

THE WAX OF FICUS GUMMIFLUA.

By F. KESSEL.

THIS wax is a chocolate colored mass, which softens when heated and melts between 60° and 70°. Boiling water extracts a considerable quantity of a brown coloring matter, leaving the wax nearly white. Boiling alcohol dissolves considerable quantities of the wax, which on cooling are redeposited in a white mass resembling cauliflower. By treatment with ether the wax may be separated into two bodies more or less soluble, the former having the composition $C_{18}H_{30}O$, and the latter, $C_{27}H_{44}O$.—*Ber. der Deutsch. Chem. Gesell.*

[Continued from SUPPLEMENT No. 180.]

RECENT SCIENCE.

NEW PRODUCTS FROM BEETS.

As the preceding notices have referred to theoretical rather than to practical subjects, it may be well to introduce an example of the value of applied science, to which attention has recently been directed by Professor Roscoe.* Modern chemistry nowhere shows to more advantage than in the utilization of waste products. Scarcely anything nowadays is allowed to run to waste. The residual substances and the by-products obtained in manufacturing operations are carefully studied by the chemist, and his studies are occasionally rewarded by the establishment of a new industry. Such has recently been the case with M. Camille Vincent, of Paris.

Since the beginning of this century the beetroot has been employed on the Continent for the preparation of sugar. Originating in Germany, the manufacture soon extended to France, where it was especially fostered by the first Napoleon in pursuance of his famous "continental system," which excluded, as far as possible, all colonial products from the French markets. To so great a magnitude has the manufacture now attained that it is said about 700,000 tons of beetroot sugar are annually manufactured in Europe.

To obtain sugar from this source, the cleansed beet is crushed, and the juice extracted by expression. This juice, having been refined and filtered, is boiled and allowed to crystallize. A sugar, identical with the ordinary product of the sugar-cane, is thus separated, while a thick, uncrystallizable sirup remains behind: this is, of course, the treacle or molasses. Beet molasses are used for sweetening purposes, or sometimes as fodder for cattle, but they are more generally employed for the preparation of a coarse spirit. To procure this spirit, the molasses, after having been diluted and acidulated, are subjected to fermentation and then to distillation. It is estimated that 100 kilogrammes of the molasses will yield about forty liters of spirit. After the distillation is completed there remains in the retort a liquid known as *vinasse*. This spent wash was formerly wasted, but it was shown many years ago by M. Dubrunfaut that it contains salts of potash. Instead, therefore, of being thrown away, it has of late years been utilized as a source of these valuable salts. The *vinasse* is evaporated to dryness and calcined, when it yields an ash termed *salin*, rich in compounds of potassium. The composition of the ash varies with the character of the soil on which it has been raised. By this process about 2,000 tons of carbonate of potash are annually produced from the French distilleries.

It might fairly be supposed that chemistry had now done its utmost to utilize the products of the beet, having obtained from it successively the sugar, the spirit, and the potash. Recent researches, however, have shown that the chemist has by no means exhausted his skill in that direction.

In the residual liquor from the distillation of the molasses there is not only the alkaline matter of the beet juice, which the root has extracted from the soil, but there is also much organic matter, some of which is nitrogenous. During the calcination of the dried *vinasse* this organic matter is decomposed, leaving a porous carbonaceous mass associated with the mineral residues. If the concentrated *vinasse* be subjected to destructive distillation in iron retorts, the volatile products of the decomposition may be secured, just as in the process of gas making. On passing these products through condensers, the condensable portions will be liquefied while the so-called permanent gases will pass outward, and may be utilized as fuel. The condensed products consist mainly of tarry and ammoniacal liquors; and in this respect they resemble the corresponding products obtained in the manufacture of coal gas, but the chemical composition of the products is not identical in the two cases. Thus the ammonia water obtained during the distillation of the *vinasse* ash contains, among other products, large quantities of the salts of trimethylamine. It is upon their presence that the new manufacture has been established.

Trimethylamine, a substance which was discovered nearly thirty years ago by Dr. Hofmann, belongs to the class of organic bodies known as "compound ammonias." Ammonia is a gaseous compound of nitrogen and hydrogen, which on solution in water forms common "spirit of hartshorn." It was shown in 1848, by M. Würtz, an eminent French chemist, that ammonia may have one of its hydrogen atoms replaced by an organic radical, like methyl. The new body thus formed is called methylamine. Pursuing this course, Dr. Hofmann showed that a second atom of hydrogen might also be replaced by methyl, and thus a body termed dimethylamine was obtained. Finally the same chemist succeeded in replacing the third, or last, atom of hydrogen in ammonia by this radical, and in this way formed trimethylamine. This compound has hitherto been regarded as nothing more than a chemical rarity; but by the new French manufacture to which we are referring, it may now be prepared commercially on an enormous scale.

Although trimethylamine is at present of no industrial value, it is far otherwise with some of its products. Thus, M. Vincent has found that its hydrochlorate may be easily decomposed by heat into free ammonia (which is, of course, a useful product), free trimethylamine (which can be again converted into its hydrochlorate), and chloride of methyl. This chloride is a combustible gaseous body, easily condensed to a mobile liquid. Hitherto it has not been obtained in quantity, but M. Vincent can now prepare it to any extent, and, condensing it in strong wrought-iron cylinders, can transport it with ease and safety.

Chloride of methyl may be advantageously used in the preparation of some of the methylated colors, such as Hofmann's violets and the aniline greens. By the newly discovered source of methyl-chloride, the cost of preparation of these colors will be economized, since it can replace the more expensive iodide. But the most interesting application of chloride of methyl which has yet been proposed is that of a refrigerating agent. By the rapid evaporation of the condensed liquid a very great reduction of temperature is produced, and as the liquid is neither poisonous nor corrosive, it promises to become of much importance. Indeed, M. Vincent has constructed a freezing machine, in which, by the evaporation of the chloride of methyl, as low a temperature as -55° centigrade may be maintained; a temperature which is considerably below the freezing point of quicksilver. We have now, therefore, in our hands a new refrigerating agent, by means of which mercury may be frozen by the pound.

CHEMISTRY OF YEAST.

In the January number of this review, we gave an account

* "On a New Chemical Industry." A Lecture delivered at the Royal Institution, on February 21, 1879, by Professor Roscoe, LL.D., F.R.S. *Nature*, No. 487, February 27, p. 398.