INDIGO AND THE VAT COLORS: FOURTH PAPER ON DYEING: BY PROFESSOR CHARLES E. PELLEW OF COLUMBIA UNIVERSITY

THE small group of colors known as the Vat colors comprise, at once, the most ancient and the most modern of all dyestuffs. The most important member of this group, indigo, has been known and used, in a more or less impure form, from the days of the ancient Egyptians. But it is only some five or six years since it was first put on the market in a perfectly pure condition. The other members of the group, the Indanthrenes, Algols, and the rest, are even more recent in origin.

The dyestuff indigo does not exist in nature as such, but is prepared, by a comparatively simple process of extraction and oxidation, from the juices of plants, the Indigoferœ, different kinds of which, Indigofera anil, I. argentea, I. tinctoria, etc., are found wild, and, up to the last few years, have been extensively cultivated in India, Java, Japan, China, Central and South America, and in Africa. Indigo may also be obtained, although in small quantities and in an impure condition, from other plants, especially from Isatis tinctoria, or woad, which at one time was extensively cultivated in England and on the continent.

The synthesis, *i. e.*, the chemical formation, of indigo from coal tar products has been justly regarded as one of the great triumphs of modern science. But let me impress upon my readers this fact—the real dyestuff, indigo, is absolutely the same material, whether it comes mixed with a great mass of impurities, as in the woad, or whether it contains from 5 to 25 per cent. of foreign matter of little or no value, as in the Bengal or natural indigo, or whether we get it from Metz or the Badische Co., chemically pure, either in the dry state or thinned with water in the form of a 20 per cent. paste. It is the same dye, and being absolutely without contamination of any kind, the artificial or synthetic dyestuff presents advantages in the matter of purity of shade, ease and surety of manipulation, and permanence of the color produced, which could never be obtained before its introduction.

Application of Indigo.—The general principles of dyeing with indigo are the same now as in the days of the Egyptians—the only difference being in the means used to bring about the chemical changes involved. Indigo itself is a blue solid, insoluble in water, acids

and alkalies, and practically unaffected by sunlight. If, however, oxygen be taken away from it, or, as the chemist would say, it is "reduced," by the action of any one of numerous deoxidizing or reducing agents, the indigo blue is changed to a new substance, indigo white, which is almost colorless, and which dissolves, in the presence of alkalies, to a bright yellow liquid. If cotton, wool, paper, wood, or indeed almost any solid materials (noticeably the fingers and nails, as some of my readers may find out), are immersed in the solution, they will absorb some of this indigo white, and then, on exposure to the air, the white indigo will rapidly take up oxygen, and become converted into the insoluble blue coloring matter.

Up to the last few years the methods used for reducing the indigo, *i. e.,* of changing the solid blue into the soluble white, were based upon some kind of fermentation, usually alcoholic fermentation. It was found out at a very early date that if indigo, ground up with water to a paste, and rendered alkaline by the addition of wood ashes, soda, or other simple alkalies, was mixed with grape juice, or any other sugary liquid, and then kept warm and allowed to ferment, the resulting liquid would contain the dyestuff dissolved in a form suitable for dyeing.

At the very best the fermentation method is slow, uncertain, and difficult to manage, especially on a small scale. In wool dyeing, to this day, vats are considerably used where syrup, ground madder root or, occasionally, woad, wheat bran, and other materials which ferment readily in the presence of alkali, are stirred up with warm water and soda, and then allowed to stand. In two or three days they are in active fermentation, and the indigo in the form of paste is added and well stirred in. After several hours more the indigo is "reduced," and, if the amount of alkali, the temperature, the concentration of the vat, and various other factors are carefully attended to, the bath can be used for several days without being made over again; fresh indigo and other ingredients being added, from time to time, as needed. Cotton, linen, wool and even silk can be dipped in this bath, which should be light greenish yellow in color, with a blue or bluish-green scum or coating, where the indigo is oxidized on the surface; and then, when the goods are taken out and exposed to the air, the blue color speedily develops.

A serious drawback to all these various fermentation vats is that a good deal of the dyestuff is always spoilt—*i. e.,* decomposed into colorless compounds which can never be regenerated or made useful. Indeed, the loss from this cause frequently amounts to 20 or 25 per cent. of all the dye used, and occasionally, especially in hot weather, far more.

Chemical Vats.—As soon as it was clearly understood just what chemical action was going on in the vats, and the object of it, chemists began to find out methods for reducing the indigo without the necessity of a long, tedious and even nasty fermentation process.

They first introduced the copperas lime vat, where the reduction was done by the use of ferrous sulphate (green vitriol or copperas), and slaked lime was used, as the alkali, to keep the indigo white dissolved.

Then they introduced zinc dust, a very powerful reducing agent, in place of the copperas, avoiding in this way the large amount of precipitated iron oxide, which always forms in the copperas vat and leads to loss of dye and muddiness and dullness of color.

Modern Methods of Dyeing Indigo.—At present, at any rate on a small scale, where the expense of the raw

material is not the very first consideration, by far the most satisfactory method is to use as a reducing agent the chemical known as sodium hydrosulphite, in a bath made strongly alkaline with caustic soda. Hydrosulphite acts very rapidly, leaving no sediment, and causes no loss or waste of the indigo; and, with its introduction, the dyeing of indigo has become extremely simple.

To still further shorten and simplify the process, the large manufacturers not only furnish indigo already ground up to a fine paste with water, but also supply indigo already reduced, by hydrosulphite or some other reducing agent, so that it is almost ready to dye with as it is, and will dissolve almost instantaneously in an alkaline bath with the addition of just a little more reducing agent. Such products are the Indigo Vat. III, Metz, and the Indigo Solution 20%, Badische. By using either of these, the preparation of a vat large enough to dye 3 or 3½ pounds of cotton is the task of but a few moments.

Dyeing Directions.—The dye pot is filled with warm water, at about 120° F. (when the finger can hardly bear the heat), and sufficient caustic soda is added to make the bath decidedly alkaline. The dyestuff is stirred into the liquid, and then to the dyestuff is added sodium hydrosulphite, in powder, or, preferably, dissolved in water, until the color of the bath changes from blue, first to green, and then to greenish yellow, with a bluish green coppery scum. If the bath is bright yellow, too much hydrosulphite has been used, and some more indigo should be added, or, if this is not desirable for fear of getting too dark shades, the bath should be exposed to the air and stirred frequently until the color is right. If the bath looks blue, or even markedly green, it needs a little more hydrosulphite. If, after reduction, the bath looks yellow but turbid, it probably needs more alkali.

Into this bath the material is placed, and stirred around until thoroughly saturated — the temperature being kept about 120° F. as far as possible. The goods are then taken out, wrung lightly by hand, and then carefully, two or three times, through the wringer to get the color evenly distributed. They are then shaken out and hung up in the air to oxidize. In half or three-quarters of an hour they should be rinsed well, in two or three waters, to get rid of all traces of the caustic alkali, and then boiled in a soap bath, to wash off the loose dyestuff and prevent rubbing. After rinsing and drying, they are ready for use.

Special Notes on Dyeing Indigo.—It is very important, when working with these Vat colors, to remember that hot solutions of caustic alkali are about as hard on the hands as any chemicals used in dyeing, and that, therefore, rubber gloves are extremely useful, if not essential. Stains left on hands, clothes and utensils, although difficult to remove by washing, are almost instantly dissolved by warm solutions of hydrosulphite with a little soda or other alkali in them.

The colors produced by synthetic indigo are clear and clean, but not brilliant. In case the slight purplish shades of natural indigo are desired, they can be obtained with special brands, Indigo R. or Indigo R. R., Metz, or by mixing some Algol Red B., Elberfeld, or Thion Indigo Red B., Kalle, with the indigo before reducing it. When dyeing to shade successive batches of materials, it is generally easier to make a strong "stock solution" of indigo reduced with hydrosulphite and alkali, and measure out the proper quantities of this standard color to be used, properly diluted with water, for each new lot of goods.

For cotton dyeing, indigo, with the

possible exception of some of the Sulphur colors, is the most permanent and valuable blue dyestuff known. Its chief drawback is a tendency to rub, especially in the darker shades. This can best be avoided by always using a bath well reduced, by washing with hot soap after each dip, and by building up the dark shades by successive dipping in moderately weak vats, rather than by getting the color once for all by using a very strong, concentrated dye-liquor.

Other Vat Colors beside Indigo.—Up to a very recent date indigo was the only dyestuff, of any interest at any rate, that was dyed in the manner just described, and produced colors fast to light and washing. During the last three or four years, however, the attention of dye chemists has been directed to this question, and at least three of the great dye houses have issued dyes which include red, brown, yellow, green, as well as different shades of blue, and which, applied in the same way as indigo, rival that color in permanence.

The class names of these colors are Indanthrene, Badische; Algol, Elberfeld; and Thion Indigo, Kalle. They are extremely interesting and valuable to the arts and crafts worker, because they are so very fast, both to light and washing. For stencil work, too, these colors, as well as the previously described Sulphur colors, will be found very valuable. But for commercial purposes they have serious disadvantages, such as high cost, difficulty in dyeing to exact shade, and, above all, difficulty in dyeing exactly even, which prevent their being adopted as freely and enthusiastically as their valuable properties would warrant.

Methods of Application.—These dyes are all applied, almost exactly like indigo, in the hydrosulphite bath, and are used for cotton and vegetable fibers, rarely for wool, silk, etc., on account of the danger to the fiber of hot caustic alkalies.

The color is always in a paste form, usually 20% strong, and therefore should be carefully shaken and mixed in the original package each time that it is used. The proper amount, to be determined only by experience, is stirred into hot water at about 140° F. if possible (this being well below a boil, and yet hot enough to scald the tips of the fingers). To this is added caustic soda, in the proportion of four or five spoonfuls of alkali to each one of the color; and when this is dissolved, the dyestuff is reduced by adding, slowly, spoonful after spoonful of sodium hydrosulphite in powder, with constant stirring, until the dyestuff is reduced. This can be tested by drawing out the dyestick, and noticing whether the liquid drops off from the end, clear or turbid. If the latter, more hydrosulphite is needed. The same test can be made by dipping a piece of white blotting paper into the liquid, and, on taking it out, noticing whether there are little spots and specks of undissolved color.

The color of some of the dyes changes when they are reduced. Thus, Indanthrene Yellow, Badische, formerly called Phenanthrene, turns from yellow to blue when enough hydrosulphite is added.

Into this hot reduced bath the well-wetted material is placed, and stirred around. After it has been thoroughly soaked through, it is kept in the bath, with constant turning, for 15 or 20 minutes, and then taken out, and run two or three times through the wringer, to get the color as even as possible. The loose dye-liquor, pressed out in this way, is returned to the dye bath, and the goods are shaken out and exposed to the air, until the color fully develops.

The free alkali should then be washed out in several waters, and, especially for the Indanthrene colors, the goods

should be passed through a very weak bath of sulphuric acid, one-half spoonful of acid to two gallons of water, after which they should be washed in hot water, and soap, till all loose color has been washed out.

The colors produced in this way are bright and interesting, especially in the reds, where the Sulphur colors are so deficient. The selected colors given below are among the very fastest known.

Badische—Indanthrene Blue, G. C. D.
" Yellow, G.
" Copper, R.
Also Indigo solution, 20%.

Elberfeld—Algol Blue, 3 G.
" Yellow.
" Red, B.

Kalle—Thion Indigo Red B.
" " Scarlet.

Metz—Indigo Vat III.

General Review of Cotton Dyeing.—The dyes hitherto described, namely, the Mineral colors, the Direct Cotton or Salt colors, the Sulphur colors, and the Vat colors, include all the important dyestuffs used for dyeing cotton and linen without the use of mordants.

In closing the subject of cotton dyeing for arts and crafts workers, it may be worth while, as a review of the subject, to publish here dyeing directions used, in actual practice, by the workers at a well-known Neighborhood House —Greenwich House—where for some years an interesting and well-managed industry has been established in home-dyed, hand-woven cotton rugs, fast to light and washing. The linen warp, loosely tied in hanks, is dyed when desired by the same formula as the filling.

In each case, the dyeing directions begin as follows: "Place goods, whether old or new, in a kettle of cold water, and boil for one hour after boiling point is reached. If dirty, boil for fifteen minutes in a weak soap bath, rinse, and boil in fresh water for one hour.

"This is to remove lime, dirt, and grease, and also to get the goods thoroughly water soaked."

DYEING DIRECTIONS

I. Manganese Brown. II. Copperas Yellow and Orange. III. Thiogene Cyanine O, Metz. IV. Indigo Blue.

I. Manganese Brown.—

- Potassium Permanganate,
- Warm water,
- Agate kettle or boiler holding 3½ gallons,
- Brown dyesticks,
- Rubber gloves.

Dissolve three tablespoonfuls of permanganate in a little warm water.

Put eleven quarts of warm water in a kettle, and add the permanganate when dissolved.

Wring out the boiled rags and dip into the liquid until thoroughly soaked. Wring tight, with wringer, if possible, and hang in the air to dry. When thoroughly dried, rinse in good hot suds and then in cold water until color stops running.

Should you wish a deeper brown, redip before drying.

The above dyes about 3 lbs. 6 oz. of rags.

II. Copperas Yellow and Orange.—

- Washing soda or soda ash,
- Copperas,
- Cold water,
- Two agate or stone kettles,
- Yellow dyesticks,
- Rubber gloves.

Put eleven quarts of cold water in each kettle. In one kettle dissolve five tablespoonfuls copperas. In the other kettle dissolve ten tablespoonfuls washing soda, or five of soda ash.

Wring out the boiled rags and dip into kettle containing the copperas, then wring out tight, shake well and dip into the kettle containing the washing soda. Wring tight again, shake out, and dry thoroughly in the air. Then wash

in good hot suds, and rinse in cold water until color stops running.

You can always get an idea of the color by wringing out a piece of the goods after dipping, and placing in the air for a few minutes; if not dark enough, redip immediately in the same baths again.

If the cloth is not wrung out dry, more water will have to be added, and the dye will lose its strength; then you must add more copperas and washing soda.

The above directions are for 10 yds. or 3 lbs. 6 oz.

Orange Color.—Same as above, only redip in solutions several times, until desired shade is obtained.

III. Thiogene Cyanine O, Metz.—

- Thiogene Cyanine O, Metz,
- Glauber's Salt crystals.
- Washing soda,
- Sodium Sulphide,
- Hot water,
- Agate kettle,
- Blue dyesticks,
- Rubber gloves.

Into ten quarts of hot water put one level teaspoonful of washing soda.

Then mix one heaping tablespoonful of Thiogene Cyanine O and one heaping tablespoonful of sodium sulphide together with a little hot water, until dye is dissolved, and add to the kettle containing the washing soda. Then put in the goods and warm thoroughly, in the dye, for fifteen minutes or so. Then add one-half tablespoonful of Glauber's salt crystals, stirring up to the boil, and let boil one-half hour or more, stirring frequently so that the goods do not get too hot, as that will darken the color. Do not put too many rags in the kettle at one time, or they will not be evenly dyed.

Wring well and hang in the air to dry. When thoroughly dried, rinse out in good hot suds, and then, again, in cold water until color stops running.

The above solution dyes about 10 oz. goods.

IV. Indigo Blue.—

- Caustic Soda,
- Indigo Blue Vat 3 (Metz),
- Hydrosulphite M L B (Metz),
- Agate or stone kettle,
- Water,
- Blue dyesticks,
- Rubber gloves.

Put eleven quarts of water in a kettle, and make it warm enough to be unbearable for the hands. Then put in eight tablespoonfuls caustic soda, and let it dissolve.

Then add one tablespoonful Indigo Blue Vat 3, Metz. Take two tablespoonfuls, or a trifle more, of Hydrosulphite M L B Powder, and slowly shake into the liquid, until liquid is green or iridescent, then try on a piece of cloth, which should be greenish yellow when taken out.

When the bath is right, immerse the goods, and stir them around for ten or fifteen minutes, until thoroughly wet with the dye liquor. Take out of the bath, wring loosely with the hand and then, carefully, two or three times with the wringer, to get the color even. Hang up in the air, well spread out, for half an hour, then rinse in two waters, wash in good hot suds, then rinse in cold water until color stops running. The goods can be dyed as well in cold water as in warm. For darker shades, redip in the same bath.

If the cloth is not wrung out dry, more water will have to be added, and the dye will lose its strength; then you must add more Hydrosulphite M L B Powder and Indigo Blue Vat 3, using your own judgment as to amount needed.

When the dye turns blue in the kettle its strength is gone. It can be regenerated by adding more Hydrosulphite M L B Powder and, perhaps, a little soda.

Always use rubber gloves when dyeing goods.

The above directions are for ten yards, or 3 lbs. 6 oz. rags.