

**DYEING** (O. Eng. *deágian*, *deáh*; Mid. Eng. *deyen*), the art of colouring textile and other materials in such a manner that the colours will not be readily removed by those influences to which they are likely to be submitted—*e.g.* washing, rubbing, light, &c. The materials usually dyed are those made from the textile fibres, silk, wool, cotton, &c., and intended for clothing or decoration; but in addition to these may be mentioned straw, fur, leather, paper, &c.

The art of dyeing dates from prehistoric times, and its practice probably began with the first dawn of civilization. Although we cannot trace the successive stages of its development from the beginning, we may suppose they were somewhat similar to those witnessed among certain uncivilized tribes to-day—*e.g.* the Maoris of New Zealand. At first the dyes were probably mere fugitive stains obtained by means of the juices of fruits, and the decoctions of flowers, leaves, barks and roots; but in course of time methods were discovered, with the aid of certain kinds of earth and mud containing alumina or iron, whereby the stains could be rendered permanent, and then it was that the true art of dyeing began. There is no doubt that dyeing was, in the early period of its history, a home industry practised by the women of the household, along with the sister arts of spinning and weaving, for the purpose of embellishing the materials manufactured for clothing.

Historical evidence shows that already at a remote period a high state of civilization existed in Persia, India, and China, and the belief is well founded that the arts of dyeing and printing have been practised in these countries during a long succession of ages. In early times the products and manufactures of India were highly prized throughout Southern Asia, and in due course they were introduced by Arabian merchants to Phœnicia and Egypt, with which countries commercial intercourse, by way of the Persian and Arabian Gulfs, seems to have existed from time immemorial. Eventually the Egyptians themselves began to practise the arts of dyeing and printing, utilizing no doubt both the knowledge and the materials derived from India. Pliny the historian has left us a brief record of the methods employed in Egypt during the first century, as well as of the Tyrian purple dye celebrated already 1000 B.C., while the chemical examination of mummy cloths by Thomson and Schunck testifies to the use by the Egyptian dyers of indigo and madder. The Phœnician and Alexandrian merchants imported drugs and dyestuffs into Greece, but we know little or nothing of the methods of dyeing pursued by

the Greeks and Romans, and such knowledge as they possessed seems to have been almost entirely lost during the stormy period of barbarism reigning in Europe during the 5th and succeeding centuries. In Italy, however, some remnants of the art fortunately survived these troublous times, and the importation of Oriental products by the Venetian merchants about the beginning of the 13th century helped to revive the industry. From this time rapid progress was made, and the dyers formed important guilds in Florence, Venice and other cities. It was about this time, too, that a Florentine named Rucellai rediscovered the method of making the purple dye orchil from certain lichens of Asia Minor. In 1429 there was published at Venice, under the title of *Mariogola dell' arte de tentori*, the first European book on dyeing, which contained a collection of the various processes in use at the time. From Italy a knowledge of dyeing gradually extended to Germany, France and Flanders, and it was from the latter country that the English king Edward III. procured dyers for England, a Dyers' Company being incorporated in 1472 in the city of London.

A new impetus was given to the industry of dyeing by the discovery of America in 1492, as well as by the opening up of the way to the East Indies round the Cape of Good Hope in 1498. A number of new dyestuffs were now introduced, and the dyewood trade was transferred from Italy to Spain and Portugal, for the East Indian products now came direct to Europe round the Cape instead of by the old trade routes through Persia and Asia Minor. Eastern art-fabrics were introduced in increasing quantity, and with them came also information as to the methods of their production. In Europe itself the cultivation of dye-plants gradually received more and more attention, and both woad and madder began to be cultivated, about 1507, in France, Germany and Holland. Under the influence of Spain the Dutch largely developed their industries and made considerable progress in dyeing. The Spaniards, on their first arrival in Mexico (1518), noticed the employment of the red dyestuff cochineal by the natives, and at once imported it to Europe, where an increasing demand for the new colouring matter gradually developed in the course of the century. A further impetus was given to the trade by the Dutch chemist Drebbel's accidental discovery, in 1630, of the method of dyeing a brilliant scarlet on wool by means of cochineal and tin solutions. The secret was soon communicated to other dyers, and the new scarlet was dyed as a speciality at the Gobelin dyeworks in Paris, and some time later (1643) at a dyeworks in Bow, near London.

In 1662 the newly established Royal Society in London took a useful step in advancing the art of dyeing, and in order to inform and assist practical dyers, caused the publication of the first original account, in the English language, of the methods employed in dyeing, entitled "An apparatus to the history of the common practices of Dyeing." Ten years later the French Minister Colbert sought to improve as well as control the operations of dyeing, by publishing a code of instructions for the use of the woollen dyers and manufacturers in France. From this time, too, a succession of eminent chemists were appointed by the French government to devote some of their attention to the study of the industrial arts, including dyeing, with a view to their progress and improvement. Dufay, Hellot, Macquer, Berthollet, Roard and Chevreul (1700–1825) all rendered excellent service to the art, by investigating the chemical principles of dyeing, by publishing accounts of the various processes in vogue, by examining the nature and properties of the dyestuffs employed, and by explaining the cause of the several phenomena connected with dyeing. With the advent of the 18th century, certain old prejudices against the use of foreign dyewoods gradually disappeared, and very rapid progress was made owing to the birth of the modern chemistry and the discovery of several useful chemical products and processes—*e.g.* Prussian Blue (1710), Saxony Blue or Indigo Extract (1740), sulphuric acid (1774), murexide (1776), picric acid (1788), carbonate of soda (1793), bleaching powder (1798). Experiments on the practical side of bleaching and dyeing were made during this period, in England by Thomas Henry, Home and Bancroft, and in France by

Dambourney, Gonfreville and others, each of whom has left interesting records of his work.

Down to the middle of the 19th century natural dyestuffs alone, with but few exceptions, were at the command of the dyer. But already in the year 1834 the German chemist Runge noticed that one of the products obtained by distilling coal-tar, namely, aniline, gave a bright blue coloration under the influence of bleaching powder. No useful colouring matter, however, was obtained from this product, and it was reserved for the English chemist Sir W. H. Perkin to prepare the first aniline dye, namely, the purple colouring matter Mauve (1856). The discovery of other brilliant aniline dyestuffs followed in rapid succession, and the dyer was in the course of a few years furnished with Magenta, Aniline Blue, Hofmann's Violet, Iodine Green, Bismarck Brown, Aniline Black, &c. Investigation has shown that the products of the distillation of coal-tar are very numerous, and some of them are found to be specially suitable for the preparation of colouring matters. Such, for example, are benzene, naphthalene and anthracene, from each of which distinct series of colouring matters are derived. In 1869 the German chemists Graebe and Liebermann succeeded in preparing Alizarin, the colouring matter of the madder-root, from the coal-tar product anthracene, a discovery which is of the greatest historical interest, since it is the first instance of the artificial production of a vegetable dyestuff. Another notable discovery is that of artificial Indigo by Baeyer in 1878. Since 1856, indeed, an ever-increasing number of chemists has been busily engaged in pursuing scientific investigations with the view of preparing new colouring matters from coal-tar products, and of these a few typical colours, with the dates of their discovery, may be mentioned: Cachou de Laval (1873); Eosin (1874); Alizarin Blue (1877); Xylidine Scarlet (1878); Biebrich Scarlet (1879); Congo Red (1884); Primuline Red (1887); Rhodamine (1887); Paranitriline Red (1889); Alizarin Bordeaux (1890); Alizarin Green (1895). At the present time it may truly be said that the dyer is furnished with quite an embarrassing number of coal-tar dyestuffs which are capable of producing every variety of colour possessing the most diverse properties. Many of the colours produced are fugitive, but a considerable number are permanent and withstand various influences, so that the general result for some years has been the gradual displacement of the older natural dyestuffs by the newer coal-tar colours.

During this period of discovery on the part of the chemist, the mechanical engineer has been actively engaged in devising machines suitable for carrying out, with a minimum of manual labour, all the various operations connected with dyeing. This introduction of improved machinery into the dyeing trade has resulted in the production of better work, it has effected considerable economy, and may be regarded as an important feature in modern dyeing.

The art of dyeing is a branch of applied chemistry in which the dyer is continually making use of chemical and physical principles in order to bring about a permanent union between the material to be dyed and the colouring matter applied. If cotton or wool is boiled in water containing finely powdered charcoal, or other insoluble coloured powder, the material is not dyed, but merely soiled or stained. This staining is entirely due to the entanglement of the coloured powder by the rough surface of the fibre, and a vigorous washing and rubbing suffices to remove all but mere traces of the colour. True dyeing can only result when the colouring matter is presented to the fibre in a soluble condition, and is then, by some means or other, rendered insoluble while it is absorbed by, or is in direct contact with, the fibre. There must always be some marked physical or chemical affinity existing between fibre and colouring matter, and this depends upon the physical and chemical properties of both. It is well known that the typical fibres, wool, silk and cotton, behave very differently towards the solution of any given colouring matter, and that the method of dyeing employed varies with each fibre. As a general rule wool has the greatest attraction for colouring matters, and dyes most readily; cotton has the least attraction, while silk occupies

in this respect an intermediate position. These differences may be to some extent due to differences of physical structure in the fibres, but they are mainly due to their different chemical composition.

On the other hand, a given fibre, *e.g.* cotton, behaves quite differently in dyeing towards various colouring matters. Some of these are not at all attracted by it, and are incapable of being used as dyestuffs for cotton. For others cotton exhibits a marked attraction, so that it is readily dyed by mere steeping in a hot solution of the colouring matter. Again, for other colouring matters cotton has little or no attraction, and cannot be dyed with them until it has been previously impregnated or prepared with a metallic salt, tannic acid or some other agent which is capable of combining with the colouring matter and precipitating it as an insoluble coloured compound within or upon the fibre. Such differences of behaviour are to be ascribed to differences in the chemical constitution or atomic arrangement of the various colouring matters.

In the case of the coal-tar colours we are, for the most part, well acquainted with their chemical constitution, and in accordance with this knowledge the chemist has arranged them in the following groups:—(1) Nitro Colours. (2) Azo Colours, including Amido-azo, Oxy-azo, Tetrazo and Polyazo Colours. (3) Hydrazone Colours. (4) Oxy-quinone Colours, including Quinone-oxime Colours. (5) Diphenylmethane and Triphenylmethane Colours, including Rosaniline, Rosolic acid and Phthaleine Colours. (6) Quinoneimide Colours, including Indamine, Indophenol, Thiazime, Thiazone, Oxazime, Oxazone, Azine, Induline, Quinoxaline and Fluorindine Colours. (7) Aniline Black. (8) Quinoline and Acridine Colours. (9) Thiazol Colours. (10) Oxy-ketone, Xanthone, Flavone and Cumarine Colours. (11) Indigo. (12) Colours of unknown constitution.

This arrangement of the colouring matters in natural chemical groups is well suited for the requirements of the chemist, but another classification is that based on the mode of their application in dyeing. This is much simpler than the previous one, and being better adapted for the practical purposes of the dyer, as well as for explaining the various methods of dyeing, it is preferred for this article. According to this arrangement colouring matters are classified under the following groups:—(1) Acid Colours. (2) Basic Colours. (3) Direct Colours. (4) Developed Colours. (5) Mordant Colours. (6) Miscellaneous Colours. (7) Mineral Colours. It is well to state that there is no sharp line of division between some of these groups, for many colours are applicable by more than one method, and might quite well be placed in two, or even three, of the above groups. This may be due either to the kind of fibre to which the colouring matter is to be applied, or to certain details in the chemical constitution of the latter which give it a twofold character.

**ACID COLOURS.**—These dyestuffs are so called because they dye the animal fibres wool and silk in an acid bath; they do not dye cotton. From a chemical point of view the colouring matters themselves are of an acid character, this being due to the presence in the molecule of nitro ( $\text{NO}_2$ ) or sulphonic acid ( $\text{HSO}_3$ ) groups. According to their origin and constitution they may be distinguished as nitro compounds, sulphonated azo compounds and sulphonated basic colours. The acid colours are usually sold in the form of their alkali salts, as variously coloured powders soluble in water. For the alkali salts in neutral or alkaline solution wool and silk have little or no affinity, but dyeing rapidly occurs if the solution is acidified with sulphuric acid whereby the colour-acid is liberated. This addition of acid, however, is necessary not only to set free the colour-acid of the dyestuff, but also to alter partially the chemical composition of the fibre, and thus render it capable of uniting more readily with the free colour-acid. It has been shown, namely, that if wool is boiled with dilute sulphuric acid, and then thoroughly washed with boiling-water till free from acid, it acquires the property of being dyed with acid colours even in neutral solution. By this treatment a portion of the wool substance is converted into so-called *lanuginic acid*, which has a strong attraction for the colour-acid of the dyestuff, with which it forms an insoluble coloured compound. For dyeing wool, the general rule is to charge the dye bath with the amount of dyestuff necessary to give the required colour, say from  $\frac{1}{2}$  to 2 or 6% on the weight of wool employed, along with 10% sodium sulphate (Glauber's salt) and 4% sulphuric acid (1.84 sp. gr.). The woollen material is then

**Classification of colouring matters.**

introduced and continually handled or moved about in the solution, while the temperature of the latter is gradually raised to the boiling point in the course of  $\frac{3}{4}$  to 1 hour; after boiling for  $\frac{1}{2}$  to  $\frac{1}{3}$  hour longer, the operation is complete, and the material is washed and dried.

In practice, modifications of this normal process may be introduced, in order to ensure the dyeing of an even colour, *i.e.* free from such irregularities as cloudiness, streaks, &c., which may be due to the quality of the material or to the special properties of the acid colour employed. Materials of a firm, close texture, also the existence of a strong affinity between fibre and colouring matter, do not generally lend themselves to the dyeing of even colours, or to a satisfactory penetration of the material. Some acid colours dye even colours without any difficulty; others, however, do not. The addition of sodium sulphate to the dyebath exerts a restraining action; the dyeing therefore proceeds more slowly and regularly, and a more equal distribution and better absorption of the colouring matter takes place. Other devices to obtain even colours are: the use of old dye-liquors, a diminished amount of acid, the employment of weaker acids, *e.g.* acetic or formic acid or ammonium acetate, and the entering of the material at a low temperature.

In the application of so-called Alkali Blue the process of dyeing in an acid bath is impossible, owing to the insolubility of the colour-acid in an acid solution. Wool and silk, however, possess an affinity for the alkali salt of the colouring matter in neutral or alkaline solution, hence these fibres are dyed with the addition of about 5% borax; the material acquires only a pale colour, that of the alkali salt, in this dyebath, but by passing the washed material into a cold or tepid dilute solution of sulphuric acid a full bright blue colour is developed, due to the liberation of the colour-acid within the fibre. In the case of other acid colours, *e.g.* Chromotrope, Chrome Brown, Chromogen, Alizarin Yellow, &c., the dyeing in an acid bath is followed by a treatment with a boiling solution of bichromate of potash, alum, or chromium fluoride, whereby the colouring matter on the fibre is changed into insoluble oxidation products or colour-lakes. This operation of developing or fixing the colour is effected either in the same bath at the end of the dyeing operation, or in a separate bath. See also *Artificial Mordant Colours*.

When dyeing with certain acid colours, *e.g.* Eosine, Phloxine and other allied bright pink colouring matters derived from resorcin, the use of sulphuric acid as an assistant must be avoided, since the colours would thereby be rendered paler and duller, and only acetic acid must be employed.

The properties of the dyes obtained with the acid colours are extremely varied. Many are fugitive to light; on the other hand, many are satisfactorily fast, some even being very fast in this respect. As a rule, they do not withstand the operations of milling and scouring very well, hence acid colours are generally unsuitable for tweed yarns or for loose wool. They are largely employed, however, in dyeing other varieties of woollen yarn, silk yarn, union fabrics, dress materials, leather, &c. Previous to the discovery of the coal-tar colours very few acid colours were known, the most important one being Indigo Extract. Prussian Blue as applied to wool may also be regarded as belonging to this class, also the purple dyestuff known as Orchil or Cudbear.

The following list includes some of the more important acid colours now in use, arranged according to the colour they yield in dyeing:—

**Red.**—Wool scarlet, brilliant scarlet, erythrine, crocein scarlet, brilliant crocein, violamine G, scarlet 3R, crystal scarlet, new coccine, chromotrope 2R, azo acid magenta, Victoria scarlet, xylidine scarlet, Palatine scarlet, Biebrich scarlet, pyrotine, orchil red, Bordeaux B, milling red, azo carmine, acid magenta, fast acid violet A 2R, naphthylamine red, fast red, claret red, eosine, erythrosine, rose Bengale, phloxine, cyanosine, cloth red, lanafuchsine, rosinduline, erio carmine.

**Orange.**—Diphenylamine orange, methyl orange, naphthol orange, crocein orange, brilliant orange, orange G, orange N, mandarin G R.

**Yellow.**—Picric acid, naphthol yellow S, fast yellow, brilliant yellow S, azoflavine, metanil yellow, resorcin yellow, tartrazine, quinoline yellow, milling yellow, azo yellow, Victoria yellow, brilliant yellow S, citronine, Indian yellow.

**Green.**—Acid green, guinea green, fast green, patent green, cyanol green, erio green, brilliant acid green 6 G.

**Blue.**—Alkali blue, soluble blue, opal blue, methyl blue, Höchst new blue, patent blue, ketone blue, cyanine, thiocarmine, fast blue, induline, violamine 3 B, azo acid blue, wool blue, indigo extract, erio glaucine, erio cyanine, erio blue, lanacyl blue, sulphon-azurine, sulphon-cyanine.

**Violet.**—Acid violet, red violet, regina violet, formyl violet, violamine B, fast violet, azo acid violet, erio violet, lanacyl violet.

**Brown.**—Fast brown, naphthylamine brown, acid brown, resorcin brown, azo brown, chrome brown, chromogene.

**Black.**—Naphthol black, azo black, wool black, naphthylamine black, jet black, anthracite black, Victoria black, azo acid black, brilliant black, union black, brilliant black B.

**BASIC COLOURS.**—These colouring matters are the salts of organic colour-bases, their name being derived from the fact that their dyeing power resides entirely in the basic part of the salt. In the free state the bases are colourless and insoluble, but in combination

with acids they form salts which are coloured and for the most part soluble in water. They are usually sold in the form of powder or crystals, the latter exhibiting frequently a beautiful metallic lustre. Wool and silk are dyed in a neutral bath, *i.e.* without any addition, the material not requiring any previous preparation. During the dyeing operation the animal fibres appear to play the part of an acid, for they decompose the colouring matter and unite with the colour-base to form an insoluble coloured salt or lake, while the acid of the colouring matter is liberated and remains in solution. Although, as a rule, a neutral dyebath is employed in dyeing wool, a slight addition (2%) of soap is sometimes made in order to give a brighter colour, while in other cases, *e.g.* with Victoria Blue, the dyebath must of necessity be made distinctly acid with acetic or sulphuric acid. Silk is usually dyed in a bath containing "boiled-off liquor" (*i.e.* the spent soap-liquor from the operation of scouring) neutralized or slightly acidified with acetic or tartaric acid. For a full colour use 2 or 3% colouring matter, enter the wool at a low temperature, heat gradually to near the boiling point in the course of  $\frac{3}{4}$  hour, and continue dyeing for  $\frac{1}{4}$  hour. Owing to the slight solubility of many basic colours, it is important to take the precaution of filtering the colour solution into the dyebath through a flannel filter, also to neutralize the alkalinity of calcareous water with a little acetic acid, to prevent decomposition of the colouring matter and precipitation of the colour-base.

Unlike the animal fibres, cotton has little or no affinity for the basic colours; hence the cotton dyer makes use of the fact that cotton has a natural attraction for tannic acid, and that the latter forms insoluble lakes with the bases of basic colours. Previous to dyeing, the cotton is prepared with tannic acid by steeping in a cold solution of the latter for several hours; cotton pieces are run at full width through a solution containing 2 to 6 oz. per gallon of tannic acid, and after being evenly squeezed are dried on steam cylinders. The cotton is then worked in a solution of tartar emetic or stannic chloride, so that the tannic acid absorbed by the fibre may be fixed upon it as insoluble tannate of antimony or tin. Although the tannic acid is thus united with metallic oxide, it still has the power of attracting the base of the colouring matter, and there is fixed upon the fibre an insoluble colour-lake, namely, a tannate of antimony and colour-base, which constitutes the dye. In this process the tannic acid is called the *mordant*, the tartar emetic acts as the *fixing-agent* for the tannic acid, and the cotton as finally prepared for dyeing is said to be *mordanted*. The proportions employed, reckoned on the weight of cotton, may vary from 2 to 10% tannic acid, or the equivalent in a decoction of sumach, myrabolans, or other tannin matter, and  $\frac{1}{2}$  to 3% tartar emetic. After mordanting and fixing of the mordant, the cotton is well washed and dyed in the cold or at 60° C. for  $\frac{1}{2}$  to 1 hour with the necessary colouring matter. Applied in this manner, basic colours are moderately fast to soap, but generally not to the action of light.

Linen is dyed in the same manner as cotton. Jute is dyed without any previous preparation, since it behaves like a tannin-mordanted fibre, attracting the basic colours direct.

The basic colours, to which class most of the earlier coal-tar colours belonged, are remarkable for their great colouring power, and in most cases for the brilliancy of the colours they yield. With the exception of certain dark colours, they are fugitive to light. It is interesting to note that only one vegetable colouring matter is at present recognized as belonging to this class, namely, the yellow dyestuff barberry bark and root (*Berberis vulgaris*) which contains the alkaloid berberine.

The following is a list of the more important basic colours derived from coal-tar:—

**Red.**—Magenta, safranine, rhodamine, pyronine red, rhoduline red, rosazein, induline scarlet.

**Orange.**—Chrysoidine, phosphine, acridine orange, tannin orange.

**Yellow.**—Auramine, benzoflavine, thioflavine T, acridine yellow, homophosphine, rhoduline yellow.

**Green.**—Malachite green, emerald green, imperial green, China green, brilliant green, Victoria green, diamond green, methylene green, azine green.

**Blue.**—Methylene blue, new methylene blue, toluidine blue, thionine blue, indamine blue, Victoria blue, night blue, Nile blue, turquoise blue, marine blue, indoine blue, metamine blue, Capri blue, indazine, metaphenylene blue, paraphenylene blue, toluylene blue, indigene, indol blue, diphen blue, setopaline, setocyanine, setoglaucine, Helvetia blue.

**Violet.**—Methyl violet, crystal violet, ethyl purple, methylene violet, mauve, paraphenylene violet, rhoduline violet, methylene heliotrope.

**Brown.**—Bismarck brown.

**Black.**—Diazine black.

**Grey.**—Methylene grey, nigrisine, new grey.

**DIRECT COLOURS.**—The characteristic feature of the dyestuffs belonging to this class is that they dye cotton "direct"—*i.e.* without the aid of mordants. Two distinct series of colouring matters of this group may be distinguished—namely, *Direct Cotton Colours* and *Sulphide Colours*.

(a) *Direct Cotton Colours.*—The colours of this class are frequently called the Substantive Cotton Colours, Benzo Colours, Diamine Colours, Congo Colours. Considered from the chemical point of

view, they are mostly alkali salts of sulphonated tetrazo colours obtained by diazotizing certain diamido compounds, e.g. benzidine, diamido-stilbene, &c., and uniting the products thus obtained with various amines or phenols. The first colouring matter of this class was the so-called Congo red, discovered in 1884, and since that time a very great number have been introduced which yield almost every variety of colour. The method of dyeing cotton consists in merely boiling the material in a solution of the dyestuff, when the cotton absorbs and retains the colouring matter by reason of a special natural affinity. The concentration of the dyebath is of the greatest importance, since the amount of colour taken up by the fibre is in an inverse ratio to the amount of dye liquor present in the bath. The addition of 1 to 3 oz. sodium sulphate and  $\frac{1}{2}$  to  $\frac{1}{3}$  oz. carbonate of soda per gallon gives deeper colours, since it diminishes the solubility of the colouring matter in the water and increases the affinity of the cotton for the colouring matter. An excess of sodium sulphate is to be avoided, otherwise precipitation of the colouring matter and imperfect dyeing result. With many dyestuffs it is preferable to use  $\frac{1}{2}$  to  $\frac{1}{3}$  oz. soap instead of soda. On cotton the dyed colours are usually not very fast to light, and some are sensitive to alkali or to acid, but their most serious defect is that they are not fast to washing, the colour tending to run and stain neighbouring fibres. Their fastness to light and washing is, however, greatly improved by a short ( $\frac{1}{2}$  hour) after-treatment with a boiling solution of copper sulphate (3%), with or without the addition of bichromate of potash (1%). Wool and silk are dyed with the direct colours either neutral or with the addition of a little acetic acid to the dyebath. On these fibres the dyed colours are usually faster than on cotton to washing, milling and light; some are very fast even to light—e.g. Diamine fast red, chrysophenine, Hessian yellow, &c. Many of the Direct Colours are very useful for dyeing plain shades on union fabrics composed of wool and cotton, silk and cotton, or wool and silk. Owing to the facility of their application, they are also very suitable for use as household dyes, especially for cotton goods.

A few vegetable dyestuffs belong to this class, notably Turmeric, saffron, annatto and safflower, but they all yield colours which are fugitive to light, and they are now of little importance. Turmeric is the underground stem or tuber of *Curcuma tinctoria*, a plant growing abundantly in the East Indies. It dyes cotton, wool and silk in a bath acidified with acetic acid or alum, yielding a bright yellow colour which is turned brown by alkalis. Saffron consists of the stigmata of the flower of *Crocus sativus*, which is grown in Austria, France and Spain. It dyes a bright orange-yellow colour. Annatto is the pulpy mass surrounding the seeds of *Bixa orellana*, a plant which grows in South America—e.g. Brazil, Cayenne, &c. It dyes cotton and silk in an alkaline or soap bath an orange colour, which is turned red by acids. Safflower consists of the dried florets of *Carthamus tinctorius*, which is grown in the East Indies, Egypt and southern Europe. Cotton is dyed a brilliant pink colour by working it in a cold alkaline (sodium carbonate) extract of the colouring matter, while gradually acidifying the solution with citric acid (lime-juice).

The Direct Colours which are derived from coal-tar products are very numerous indeed; they are largely employed, and occupy a very important position among dyestuffs. The following list includes the principal coal-tar colours of this group:—

**Red.**—Congo red, brilliant Congo, benzopurpurine, brilliant purpurine, deltapurpurine, diamine scarlet, diamine fast red, rosaurine, salmon red, erica, Titan pink, St Denis red, Columbia red, naphthylene red, Congo rubine, acetopurpurine, dianol red, thiamine crimson, geranine, brilliant geranine, Columbia fast scarlet, benzo fast scarlet, thiamine red, diamine rose, Dongola red, rosophenine.

**Orange.**—Congo orange, benzo orange, toluylene orange, mikado orange, brilliant orange, Columbia orange, diamine orange, pyramine orange, benzo fast orange.

**Yellow.**—Chrysamine, cresotin yellow, diamine yellow, carbazol yellow, chrysophenine, Hessian yellow, curcumin yellow, thiazol yellow, thioflavine S, oriol, mimosa yellow, Columbia yellow, cotton yellow, chloramine yellow, direct yellow, diamine fast yellow, diamine gold, sun yellow, stilbene yellow, chlorophenine, oxyphenine.

**Green.**—Benzo olive, Columbia green, benzo green, diamine green, direct green, diphenyl green, oxamine green, eboli green.

**Blue.**—Azo blue, benzoazurine, brilliant azurine, sulphon-azurine, diamine blue, benzo indigo blue, benzo black blue, Chicago blue, Columbia blue, Erie blue, Zambezi blue, benzo cyanine, Congo blue, diamine sky blue, brilliant benzo blue, benzo chrome black blue, oxamine blue, diphenyl blue, diamineral blue, diaminogene, benzo fast blue, diazo indigo blue, brilliant chlorazol blue.

**Violet.**—Hessian purple, Congo Corinth, heliotrope, Congo violet, diamine violet, Hessian violet, azo violet, benzo violet, violet black, diamine Bordeaux, chlorantine lilac, diphenyl violet, triazol violet, Columbia violet.

**Brown.**—Benzo brown, Congo brown, toluylene brown, diamine brown, cotton brown, Hessian brown, terra-cotta, mikado brown, catechu brown, wool brown, Columbia brown, Zambezi brown, benzo chrome brown, direct fast brown, direct bronze brown, chloramine brown, triazol brown, toluylene brown, dianol brown, Crumpsall direct fast brown.

**Black.**—Diamine black, Columbia black, Nyanza black, Tabora black, Zambezi black, chromanil black, benzo black, benzo fast

black, direct blue black, Pluto black, oxydiamine black, diamine jet black, polyphenyl black, union black, triazol black, Titan black, cotton black, oxamine black.

**Grey.**—Benzo grey, benzo black, azo mauve, diaminogene, neutral grey.

(b) **Sulphide Colours.**—These dyestuffs are only suitable for dyeing the vegetable fibres, since they must be applied in a strongly alkaline bath. The dyestuff Cachou de Laval, discovered in 1873, was the first member of this group, and was obtained by melting a mixture of sodium sulphide and various organic substances—e.g. bran, sawdust, &c. In recent years numerous other dyestuffs have been added to the list, namely, grey, blue, green, brown, and especially black colours, by submitting certain definite amido compounds of the aromatic series to a similar treatment with sodium sulphide or sodium thiosulphate, and subsequent oxidation. The mode of dyeing with these colours is based on the fact that they are soluble in an alkaline reducing agent, and if the cotton is worked in the solution, subsequent oxidation develops the colour, which is fixed upon the fibre in an insoluble condition. The material is boiled for about one hour in a solution of the colour (10 to 15%), with the addition of sodium carbonate (1 to 10%), common salt (10 to 20%), and sodium sulphide (5 to 30%); it is then washed in water, and may be developed by heating in a bath containing 2 to 5% of bichromate of soda, and 3 to 6% acetic acid. A final washing with water containing a little soda to remove acidity is advisable. The sulphide colours are remarkable for their fastness to light, alkalis, acids and washing, but unless proper care is exercised the cotton is apt to be tendered on being stored for some time.

The following list includes some of the most important of the colours of this class:—

**Yellow.**—Immedial yellow, pyrogene yellow, sulphur yellow, thion yellow, thiogene yellow.

**Orange.**—Eclipse phosphine, immedial orange, pyrogene orange, thion orange, thiogene orange.

**Green.**—Pyrogene green, Italian green, eclipse green, pyrol green, immedial green, katigene green, thionol green.

**Blue.**—Immedial blue, immedial sky blue, eclipse blue, katigene indigo, pyrogene blue, sulphur blue, thion blue, thiogene blue.

**Violet.**—Katigene violet, thiogene heliotrope, thiogene purple.

**Brown.**—Pyrogene brown, pyrogene yellow, Cachou de Laval, thiocatechine, katigene black brown, eclipse brown, immedial brown, katigene brown, dianol brown.

**Grey and Black.**—Pyrogene grey, Vidal black, immedial black, katigene black, anthraquinone black, St Denis black, amidazol black, cross dye black, eclipse black, carbide black, thiogene black, sulphaniline black, sulfogene black, pyrogene black, dianol black, sulphur black, thion black, kryogene black.

This class of colours is continually increasing in number, and for certain purposes in cotton dyeing the group has acquired great importance.

**DEVELOPED COLOURS.**—This group includes certain azo colours which are developed or produced upon the fibre itself (usually cotton) by the successive application of their constituent elements. It may be conveniently divided into the following sub-groups:—Insoluble Azo Colours, Developed Direct Colours, Benzo Nitro Colours.

(a) The **Insoluble Azo Colours** are produced as insoluble coloured precipitates by adding a solution of a diazo compound to an alkaline solution of a phenol, or to an acid solution of an amido compound. The necessary diazo compound is prepared by allowing a solution containing nitrous acid to act upon a solution of a primary aromatic amine. It is usually desirable to keep the solutions cool with ice, owing to the very unstable nature of the diazo compounds produced. The colour obtained varies according to the particular diazo compound, as well as the amine or phenol employed,  $\beta$ -naphthol being the most useful among the latter. The same coloured precipitates are produced upon the cotton fibre if the material is first impregnated with an alkaline solution of the phenol, then dried and passed into a cold solution of the diazo solution. The most important of these colours is *para-nitraniline red*, which is dyed in enormous quantities on cotton pieces. The pieces are first "prepared" by running them on a padding machine through a solution made up of 30 grms.  $\beta$ -naphthol, 20 grms. caustic soda, 50 grms. Turkey red oil, and 5 grms. tartar emetic in 1000 grms. (1 litre) water. They are then dried on the drying-machine, and are passed, after being allowed to cool, into the diazo solution, which is prepared as follows: 15 grms. *para-nitraniline* are dissolved in 53 c.c. hydrochloric acid (34° Tw.) and a sufficiency of water. To the cold solution a solution of 10½ grms. sodium nitrite is added while stirring. The whole is then made up to 1200 c.c., and just before use 60 grms. sodium acetate are added. The colour is developed almost immediately, but it is well to allow the cotton to remain in contact with the solution for a few minutes. The dyed cotton is squeezed, washed, soaped slightly, and finally rinsed in water and dried. A brilliant red is then obtained which is fast to soap but not to light. If the *para-nitraniline* used in the foregoing process is replaced by *meta-nitraniline*, a yellowish-orange colour is obtained; with  $\alpha$ -naphthylamine, a claret-red; with amido-azo-toluene, a brownish red; with benzidine, a dark chocolate; with dianisidine, a dark blue; and so on. The dyed colours are fast to washing and are much used in practice, particularly the

paranitraniline red, which serves as a substitute for Turkey-red, although it is not so fast to light as the latter.

(b) *Developed Direct Colours*.—The primuline colours were the first representatives of this class and are derived from the yellow dyestuff known as primuline, which dyes cotton in the same manner as the direct colours. The primuline yellow thus obtained is fugitive to light and of little practical value, but since the colouring matter is an amido base it can be diazotized in the fibre and then developed in solutions of phenols or amines, whereby azo dyes of various hues may be obtained, according to the developer employed; thus,  $\beta$ -naphthol develops a bright red colour, resorcin develops an orange, phenol a yellow, naphthylamine a brown, &c. The dyeing of the primuline yellow is effected by boiling the cotton for one hour in a solution of primuline (5%) and common salt (10 to 20%). The diazotizing operation consists in passing the dyed and rinsed cotton for 5 to 10 minutes into a cold solution of nitrous acid—i.e. a solution of  $\frac{1}{2}$  oz. sodium nitrite per gallon of water, slightly acidified with sulphuric acid. The diazotized material should not be exposed to light, but at once washed in cold water and passed into the developer. The developing process consists in working the diazotized material for 5 to 10 minutes in a cold solution of the necessary phenol, and finally washing with water. The only developer of any practical importance is a solution of  $\beta$ -naphthol in caustic soda, which produces primuline red. The primuline colours are best adapted for cotton dyeing, and the colours obtained are fast to washing and to moderate soaping, but they are not very fast to light.

If cotton is dyed with other direct colours containing free amido groups, the colour can be diazotized on the dyed fibre exactly in the same manner as in the case of primuline-dyed cotton, and then developed by passing into the solution of an amine or phenol, or by treating it with a warm solution of sodium carbonate. In this manner a new azo dye is produced upon the fibre, which differs from the original one not only in colour, but also by being faster to washing and other influences. A treatment with copper sulphate solution after development is frequently beneficial in rendering the colour faster to light. Some Direct Colours, indeed, are of little value, owing, for example, to their sensibility to acids, until they have been diazotized and developed, the usual developers being  $\beta$ -naphthol, resorcinol, phenol and phenylene-diamine.

The following Direct Colours, after being applied to cotton, may be submitted to the above treatment, the colours produced being chiefly blue, brown and black:—

*Blue*.—Diazurine, diazo blue, diamine blue, diaminogene.

*Red*.—Rosanthiene.

*Brown*.—Diazo brown, diamine cutch, diamine brown, cotton brown.

*Grey and Black*.—Benzo blue, diazo blue black, diazo black, diamine black, diazo brilliant black.

(c) *Benzo Nitrol Colours*.—These are certain Direct Colours, dyed on cotton in the ordinary manner, which are then developed by passing into a diazo solution—e.g. diazotized para-nitraniline, &c. The dyed colour here plays the part of a phenol or amine, and reacts with the diazo compound to produce a new colour. The process is similar to the production of the Insoluble Azo Colours, the  $\beta$ -naphthol which is there applied to the fibre being here replaced by a Direct Colour. The colour of the latter is rendered much deeper by the process, and also faster to washing and to the action of acids. The dyestuffs recommended for application in the manner described are: Benzo nitrol brown, toluylene brown, direct fast brown, Pluto black, direct blue black.

"*Topping*" Direct Colours.—The direct colours possess the remarkable property of precipitating the basic colours from aqueous solution. Use is frequently made of this property for "topping" cotton dyed with direct colours either with a view to obtain compound shades or to brighten the colour. Thus by dyeing cotton first yellow in chrysamine and then dyeing it again in a cold bath of methylene blue a brilliant shade of green results. If, on the other hand, a direct blue is topped with methylene blue, its brilliancy may be enhanced.

**MORDANT COLOURS**.—The colouring matters of this class include some of the most important dyestuffs employed, since they furnish many colours remarkable for their fastness to light, washing and other influences. Employed by themselves, Mordant Colours are usually of little or no value as dyestuffs, because, with few exceptions, either they are not attracted by the fibre, particularly in the case of cotton, or they only yield a more or less fugitive stain. Their importance and value as dyestuffs are due to the fact that they act like weak acids and have the property of combining with metallic oxides to form insoluble coloured compounds termed "lakes," which vary in colour according to the metallic oxide or salt employed. The most stable lakes are those in which the colouring matter is combined with two metallic oxides, a sesquioxide and a monoxide—e.g. alumina and lime. In applying colouring matters of this class the object of the dyer is to precipitate and fix these coloured lakes upon and within the fibre, for which purpose two operations are necessary, namely, mordanting and dyeing.

The mordanting operation aims at fixing upon the fibre the necessary metallic oxide or insoluble basic salt, which is called the mordant, although the term is also applied to the original metallic salt employed. In the subsequent dyeing operation the mordanted material

is boiled with a solution of the colouring matter, during which the metallic oxide attracts and chemically combines with the colouring matter, producing the coloured lake *in situ* on the fibre, which thus becomes dyed. The mode of applying the mordants varies according to the nature of the fibre and the metallic salt employed, the chief mordants at present in use being salts of chromium, aluminium, tin, copper and iron. The method of mordanting wool depends upon its property of decomposing metallic salts, and fixing upon itself an insoluble metallic compound, when boiled in their solutions. This decomposition is facilitated by the heating and by the dilution of the solution, but it is chiefly due to the action of the fibre itself. The exact nature of the substance fixed upon the fibre has not in all cases been determined; probably it is a compound of the metallic oxide with the wool-substance itself, which has the character of an amido-acid. The mordant most largely employed for wool is bichromate of potash, since, besides being simply applied, and leaving the wool with a soft feel, it yields with the various mordant-dyestuffs a large variety of fast colours. The wool is boiled for 1 to 1½ hours in a solution containing 2 to 3% bichromate of potash on the weight of the wool employed. During this operation the wool at first attracts chromic acid, which is gradually reduced to chromium chromate, so that the mordanted fibre has finally a pale olive-yellow tint. In the dyebath, under the influence of a portion of the dyestuff, further complete reduction to chromic hydrate occurs before it combines with the colouring matter. Not unfrequently certain so-called "assistants" are employed in small amount along with the bichromate of potash—e.g. sulphuric acid, cream of tartar, tartaric acid, lactic acid, &c. The use of the organic acids here mentioned ensures the complete reduction of the chromic acid on the wool to chromic hydrate already in the mordant bath, and the pale greenish mordanted wool is better adapted for dyeing with colours which are susceptible to oxidation—e.g. alizarin blue. For special purposes chromium fluoride, chrome alum, &c., are employed. Alum or aluminium sulphate (8%), along with acid potassium tartrate (cream of tartar) (7%), is used for brighter colours—e.g. reds, yellows, &c. The object of the tartar is to retard the mordanting process and ensure the penetration of the wool by the mordant, by preventing superficial precipitation through the action of ammonia liberated from the wool; it ensures the ultimate production of clear, bright, full colours. For still brighter colours, notably yellow and red, stannous chloride was at one time largely employed, now it is used less frequently; and the same may be said of copper and ferrous sulphate, which were used for dark colours. *Silk* may be often mordanted in the same manner as wool, but as a rule it is treated like cotton. The silk is steeped for several hours in cold neutral or basic solutions of chromium chloride, alum, ferric sulphate, &c., then rinsed in water slightly, and passed into a cold dilute solution of silicate of soda, in order to fix the mordants on the fibre as insoluble silicates. Cotton does not, like wool and silk, possess the property of decomposing metallic salts, hence the methods of mordanting this fibre are more complex, and vary according to the metallic salts and colouring matters employed, as well as the particular effects to be obtained. One method is to impregnate the cotton with a solution of so-called "sulphated oil" or "Turkey-red oil"; the oil-prepared material is then dried and passed into a cold solution of some metallic salt—e.g. aluminium acetate, basic chromium chloride, &c. The mordant is thus fixed on the fibre as a metallic oleate, and after a passage through water containing a little chalk or silicate of soda to remove acidity, and a final rinsing, the cotton is ready for dyeing. Another method of mordanting cotton is to fix the metallic salt on the fibre as a tannate instead of an oleate. This is effected by first steeping the cotton in a cold solution of tannic acid or in a cold decoction of some tannin matter, e.g. sumach, in which operation the cotton attracts a considerable amount of tannic acid; after squeezing, the material is steeped for an hour or more in a solution of the metallic salt, and finally washed. The mordants employed in this case are various—e.g. basic aluminium or ferric sulphate, basic chromium chloride, stannic chloride (cotton spirits), &c. There are other methods of mordanting cotton besides those mentioned, but the main object in all cases is to fix an insoluble metallic compound on the fibre. It is interesting to note that whether the metallic oxide is united with the substance of the fibre, as in the case of wool and silk, or precipitated as a tannate, oleate, silicate, &c., as in the case of cotton or silk, it still has the power of combining with the colouring matter in the dyebath to form the coloured "lake" or dye on the material.

The dyeing operation consists in working the mordanted material in a solution of the necessary colouring matter, the dyebath being gradually raised to the boiling point. With many colouring matters, e.g. with alizarin, it is necessary to add a small percentage of calcium acetate to the dyebath, and also acetic acid if wool is being dyed. In wool-dyeing, also, the mordanting operation may follow that of dyeing instead of preceding it, in which case the boiling of the wool with dyestuff is termed "stuffing," and the subsequent developing of the colour by applying the mordant is termed "saddening," because this method has in the past been usually carried out with iron and copper mordants, which give dull or sad colours. The method of "stuffing and saddening" may, however, be carried out with other mordants, even for the production of bright colours, and it is now frequently employed with certain alizarin dyestuffs

for the production of pale shades which require to be very even and regular in colour. There is still another method of applying Mordant Colours in wool-dyeing, in which the dyestuff and the mordant are applied simultaneously from the beginning; it is known as the "single-bath method." It is only successful, however, in the case of certain colouring matters and mordants, to some of which reference will be made in the following paragraphs.

*The Natural Mordant Colours.*—It is interesting to note that nearly all the natural or vegetable dyestuffs employed belong to the class of Mordant Colours, the most important of these being included in the following list:—*Madder, Cochineal, Peachwood, Sapanwood, Limarwood, Camwood, Barwood, Sanderswood, Old Fustic, Young Fustic, Quercitron Bark, Persian Berries, Weld, Logwood.*

*Madder* consists of the dried ground roots of *Rubia tinctorum*, a plant of Indian origin. Formerly cultivated largely in France and Holland, it was long one of the most important dyestuffs employed, chiefly in the production of Turkey-red and in calico-printing, also in wool-dyeing. With the different mordants it yields very distinct colours, all fast to light and soap, namely, red with aluminium, orange with tin, reddish brown with chromium, purple and black with iron. *Madder* contains two closely allied colouring matters, namely, alizarin and purpurin. The former, which is by far the more important, is now prepared artificially from the coal-tar product anthracene, and has almost entirely superseded *madder*.

*Cochineal* is the dried scale-insect *Coccus cacti*, which lives on certain of the cactus plants of Mexico and elsewhere. The rearing of cochineal was once a large and important industry, and although still pursued, it has seriously declined, in consequence of the discovery of the azo scarlets derived from coal-tar. The colouring matter of cochineal, carminic acid, is believed by chemists to be a derivative of naphthalene, but its artificial production has not yet been accomplished. *Cochineal* dyes a purple colour with chromium mordant, crimson with aluminium, scarlet with tin, and grey or slate with iron. Its chief employment is for the purpose of dyeing crimson, and more especially scarlet, on wool. Crimson is dyed by mordanting the wool with alum and tartar and dyeing in a separate bath with ground cochineal. Scarlet on wool is obtained by the single-bath method, namely, by dyeing the wool with a mixture of stannous chloride (or nitrate of tin), oxalic acid, and cochineal. It is usual to add also a small amount of the yellow dyestuff flavine in order to obtain a yellower shade of scarlet. The cochineal colours are very fast to light, but somewhat susceptible to the action of alkalis.

*Peachwood, Sapanwood* and *Limarwood* are usually referred to as the "soluble red-woods," because of the solubility in water of the colouring principle they contain. They consist of the ground wood of various species of *Caesalpinia* found in Central America, the East Indies and Peru. They all yield more or less similar colours with the different mordants—claret-brown with chromium, red with aluminium, bright red with tin, dark slate with iron. Owing to the fugitive character of all the colours to light, these dyewoods are now comparatively little employed in dyeing.

*Camwood, Barwood* and *Sanderswood* represent the so-called "insoluble red-woods," their colouring principles being sparingly soluble even in boiling water. They are obtained from certain species of *Pterocarpus* and *Baphia*, large trees growing in the interior of West Africa. Their general dyeing properties are similar, a claret-brown being obtained with chromium mordant, a brownish red with aluminium, a brighter red with tin, and purplish brown with iron. Their chief employment is in wool-dyeing, for the production of various shades of brown, being best applied by the "stuffing and saddening" method above described; but since the colours are fugitive to light, they are now very largely replaced by alizarin. A brown on wool is obtained by first boiling for one to two hours in a decoction of the ground wood (50%), and then boiling in a separate bath in solution of bichromate of potash (2%) for half an hour. These dye-woods are also employed by the indigo-dyer, in order to give a brownish ground colour to the wool previous to dyeing in the indigo vat, and thus obtain a deeper, fuller blue. The colouring matters contained in these dyewoods have not been exhaustively examined.

*Fustic* is a yellow dyestuff, and consists of the wood of the dyer's mulberry tree, *Morus tinctoria*, which grows in Cuba, Jamaica, &c. It is still an important and largely used dyestuff, being cheap, and the colours obtained from it being satisfactorily fast to light and other influences. With chromium mordant it yields an olive-yellow or "old-gold" shade; with aluminium, yellow; with tin, a brighter yellow; with iron, an olive-green. It is chiefly employed in wool-dyeing along with other dyestuffs, and furnishes the yellow in compound shades. Two colouring principles exist in Old Fustic, namely, morin and maclurin, the former being the most important, and generally regarded as the true colouring matter.

*Quercitron Bark* consists of the inner bark of an oak-tree, *Quercus tinctoria*, which grows in the North American States. It dyes somewhat like Old Fustic, but gives with aluminium and tin mordants brighter yellows, for which colours it is chiefly used. The colouring principle of Quercitron Bark is called quercitrin, which by the action of boiling mineral acid solutions is decomposed, with the production of the true colouring matter termed quercetin.

So-called *Flavine* is a commercial preparation of Quercitron Bark consisting of quercitrin or of quercetin; it is much used by wool-dyers for the production of bright yellow and orange colours. Wool is dyed in single bath by boiling with a mixture of Flavine (8%), stannous chloride (4%) and oxalic acid (2%). Flavine is used in small quantity along with cochineal for dyeing scarlet on wool.

*Persian Berries* are the dried unripe fruit of various species of *Rhamnus* growing in the Levant. The general dyeing properties are similar to those of Quercitron Bark, the orange colour given with tin mordant being particularly brilliant. The high price of this dyestuff causes its employment to be somewhat limited. The colouring matter of Persian Berries is called xanthorhamnin, which by the action of fermentation and acids yields the true dyestuff rhamnetin.

*Weld* is the dried plant *Reseda luteola*, a species of wild mignonette, formerly largely cultivated in Europe. Its dyeing properties resemble those of Quercitron Bark, but the yellows with aluminium and tin mordants are much brighter and purer, and also faster to light. It is still used to a limited extent for dyeing a bright yellow on woollen cloth and braid for the decoration of military uniforms. Quite recently the colouring matter of Weld, namely, luteolin, has been prepared artificially, but the process is too expensive to be of practical use.

*Logwood* is the heart-wood of *Haematoxylon campechianum*, a tree growing in Central America. It is the most important natural dyewood at present employed, being largely used for dyeing dark blues and black on silk, wool and cotton. With chromium and aluminium mordants logwood dyes a dark blue, and even black; with tin, a dark purple; and with iron, black. The colours are only moderately fast to light. On wool the mordant is bichromate of potash; on cotton and silk an iron mordant is employed. Before use by the dyer the logwood is ground and aged or oxidized, by allowing moistened heaps of the ground wood to ferment slightly, and by frequently turning it over to expose it freely to the air. By this means the colouring principle haematoxylin which logwood contains is changed into the true colouring matter haematein. The constitution of this colouring matter has been recently discovered; it is very closely allied to the brazilin of peachwood, sapanwood and limarwood, and is also a member of the  $\gamma$ -pyrone group of colouring matters.

The importance of the above-mentioned natural dyestuffs is gradually diminishing in favour of mordant dyestuffs and others derived from coal-tar. Fustic and logwood are perhaps the most largely used, and may continue to be employed for many years, no satisfactory artificial substitutes having hitherto come into the market.

The *Artificial Mordant Colours* are well represented by alizarin, the colouring matter of the madder root, which was the first natural dyestuff prepared artificially from the coal-tar product anthracene (1868). For this reason many of these colours are frequently referred to as the Alizarin Colours. At the present time, however, there are numerous Mordant Colours which are prepared from other initial materials than anthracene; they are not chemically related to alizarin, and for these the term Alizarin Colours is therefore inappropriate. The property, which Mordant Colours possess in common, of combining with metals and producing lakes, which readily adhere to the fibre, depends upon their chemical constitution, more particularly upon the general and relative position in the molecule of certain side atomic groups. In alizarin there are, for example, two characteristic hydroxyl groups (OH) occupying a special (ortho) position in the molecule, *i.e.* they are next to each other, and also next to one of the so-called ketone groups (C:O). In other Mordant Colours there are carboxyl (COOH) as well as hydroxyl groups, which are all-important in this respect. In addition to this, the general dyeing property is influenced by the constitution of the molecule itself, and by the presence of other side-groups, *e.g.* NH<sub>2</sub>, HSO<sub>3</sub>, &c., which modify the colour as to solubility or hue. Hence it is that the members of this group, while possessing the mordant-dyeing property in common, differ materially in other points. Some, like alizarin, are not in themselves to be regarded as colouring matters; but rather as colouring principles, because they only yield useful dyes in combination with metallic oxides. According to their constitution, these may yield one or many colours with the various metallic oxides employed, and they are used for cotton as well as for wool and silk. Other Mordant Colours, *e.g.* many of the Direct Colours and others, are capable of dyeing either the vegetable or animal fibres without the aid of a mordant; they are fully developed colouring matters in themselves, and possess the mordant-dyeing property as an additional feature, in consequence of the details of their chemical constitution, to which reference has been made in the foregoing paragraphs. As a rule these yield, at most, various shades of one colour with the different oxides, and are only suitable for the animal fibres, particularly wool.

In the following list, the most important artificial Mordant Colours are arranged according to the colour they give in conjunction with the aluminium mordant, unless otherwise indicated. Some of those named here dye the animal fibres, even without mordants; some are Direct Colours possessing mordant-dyeing

properties, others are sulphonic acid derivatives of Alizarin Colours, suitable for wool but not for cotton.

**Red.**—Alizarin, anthrapurpurin, flavopurpurin, purpurin, alizarin Bordeaux, alizarin garnet R, alizarin maroon, alizarin S, cloth red, diamine fast red, anthracene red, chrome red, chrome Bordeaux, salicine red, erio chrome red, emin red, milling red.

**Orange and Yellow.**—Alizarin orange, alizarin orange G, alizarin yellow paste, alizarin yellow A, alizarin yellow C, anthracene yellow, galloflavin, alizarin yellow GG, alizarin yellow R, diamond flavin G, chrome yellow D, Crumpsall yellow, fast yellow, diamond yellow, benzo orange R, cloth orange, carbazol yellow, chrysamine, milling orange.

**Green.**—Coerulein, coerulein S, alizarin green S, fast green (Fe), naphthol green (Fe), Dioxin (Fe), Gambine (Fe), azo green, gallanil green, alizarin green G and B, acid alizarin green, alizarin cyanine green, alizarin viridine, diamond green, chrome green, Domingo green.

**Blue.**—Alizarin blue, alizarin blue S, alizarin cyanine, anthracene blue, brilliant alizarin blue, alizarin indigo blue S, gallanilic indigo, acid alizarin blue, brilliant alizarin cyanine, alizarin grisole, alizarin sky blue, alizarin saphirole, gallanilide blue, delphine blue, gallamine blue, celestine blue, chrome blue, gallazine A, phenocyanine, coreine.

**Purple and Violet.**—Gallein, alizarin heliotrope, anthraquinone violet, chrome prime, gallocyanine, chrome violet, anthracene chrome violet.

**Brown.**—Anthracene brown, chromogen, cloth brown, diamond brown, alizarin brown, fast brown, alizarin acid brown, chrome brown, palatine chrome brown, erio chrome brown.

**Black.**—Alizarin black, diamond black, alizarin blue black, alizarin cyanine black, alizarin fast grey, chromotrope, chrome black, erio chrome black, anthracite black, acid alizarin black, anthracene chrome black.

A brief description of the application of a few of the more important of the above colouring matters will suffice.

*Alizarin*, *Anthrapurpurin* and *Flavopurpurin* give somewhat similar shades with the different mordants, namely, brown with chromium, red with aluminium, orange with tin, and purple with iron.

In wool-dyeing they are applied along with other Mordant Colours on chromium mordant for the production of a large variety of compound shades, browns, drabs, greys, &c., the presence of acetic acid in the dyebath being advantageous. When alum and tartar mordant is employed, for the production of reds, it is necessary to add a small amount (4%) of calcium acetate to the dyebath, in order to neutralize the strong acidity of the mordanted wool, and to furnish the calcium of the colour-lake fixed upon the fibre, which is regarded as an aluminium-calcium compound of the colouring matter.

In cotton-dyeing the above colouring matters are chiefly used for the production of so-called Turkey-red, a colour remarkable for its brilliancy and its fastness to light and soap. These properties are due to the preparation of the cotton with oil, in addition to the ordinary mordanting and dyeing, whereby there is fixed on the fibre a permanent and stable lake, in which aluminium and calcium are combined with alizarin and some form of fatty oxy-acid. In the older processes employed, the preparation of the cotton with oil was effected by passing the material several times through emulsions of olive oil and potassium carbonate solution; at a later date, and even now in the case of cloth, the cotton is first impregnated with hot oil (Steiner's process), then passed through solutions of alkali carbonate. After the preparation with oil or oil-emulsions, the cotton is "stoved," *i.e.* heated for several hours in special chambers or stoves to a temperature of about 70° C., during which operation the oil is decomposed and oxidized and becomes indelibly attached to the fibre. The oil-prepared cotton is steeped in cold solutions of basic aluminium sulphate or acetate, washed, dyed with alizarin, and finally boiled for several hours with soap solution under pressure in order to brighten the colour. In the more recent and much more expeditious "sulphated-oil process," castor oil is employed instead of olive oil, and before use it is submitted to a treatment with sulphuric acid, the sulphated oil thus obtained being finally more or less neutralized with alkali. The cotton is impregnated with this sulphated-oil solution, dried, mordanted with aluminium acetate, dyed, dried, steamed and soaped. The operation of steaming plays an important part in brightening and fixing the colour-lake on the fibre. In these and all other Turkey-red processes, the oil, probably in the form of a fatty oxy-acid, acts as a fixing agent for the aluminium and enters into the composition of the red lake, imparting to it both brilliancy and permanency.

*Alizarin S* is a sulphonic acid derivative of alizarin, and since it is much more soluble, it readily yields level colours. Silk is dyed in a similar manner to wool, the fibre being mordanted by the ordinary methods and then dyed in a separate bath.

*Diamine Fast Red* is applied to cotton as a Direct Colour, with the addition of soda or soap to the dyebath. By treating the dyed colour with a solution of fluoride of chromium, its fastness to washing is materially increased. Wool is dyed in a similar manner, sodium sulphate being added to the dyebath, and the dyed colour treated with fluoride of chromium or bichromate of potash. On wool, the colour is so extremely fast to light and to milling that it may well serve as a substitute for alizarin.

*Alizarin Orange* is employed in the same manner as alizarin. In wool-dyeing it is usually applied on chromium mordant for browns and a variety of compound shades in combination with other Alizarin Colours and dyewood extracts, less frequently on aluminium mordant.

*Galloflavin* is used in wool and silk dyeing on chromium mordant as a substitute for fustic and other yellow dyewoods, to furnish the yellow part of compound shades.

The alizarin yellows, R and GG, anthracene yellow, diamond flavine, chrome yellow, diamond yellow, carbazol yellow, chrysamine, &c., are Direct Colours with mordant-dyeing properties. They also serve as substitutes for fustic in wool or silk dyeing, and are dyed either on a chromium mordant, or first in an acid bath and afterwards saddened with bichromate of potash.

*Coerulein* is employed in dyeing wool, silk or cotton with aluminium or chromium mordants, either as a self-colour or for compound shades. With aluminium mordant the colour is a moderately bright green, more particularly on silk; with chromium mordant, an olive-green. *Coerulein S* is the more soluble bisulphite compound of the ordinary coerulein. It is applied in the same manner, care being taken, however, to dye for some time (one hour) at a temperature not exceeding 60° C. until the bath is nearly exhausted, and then only raising the temperature to the boiling point. Without this precaution coerulein S is decomposed, and the ordinary insoluble coerulein is precipitated. The colours obtained are very fast to light.

*Fast Green*, *Dioxine* and *Gambine* are chiefly of use in calico-printing and in wool-dyeing. With iron mordant they yield olive-greens, which on wool are extremely fast to light. Cotton is impregnated with ferrous acetate, dried, aged and fixed with silicate of soda, then dyed in a neutral bath. Wool is mordanted with ferrous sulphate and tartar (3% of each) and dyed in a neutral bath.

*Acid Alizarin Green*, *Alizarin Cyanine Green* and *Diamond Green* all dye wool direct in a bath acidified with acetic or sulphuric acid, and the dyed colour may be afterwards fixed or saddened with bichromate of potash, or they may be dyed on chromium-mordanted wool. The first method is very useful for pale shades, since the colours are very level or regular.

*Alizarin Blue* is a dark blue dyestuff which, owing to the fastness of the colours it yields, has for many years been regarded as a worthy substitute for indigo in wool-dyeing. It is applied in the same manner as alizarin, the chromium mordant being alone employed. *Alizarin blue S* is the soluble sodium bisulphite compound of alizarin blue; it corresponds, therefore, to the above-mentioned coerulein S, and in its application the same precautions as to the temperature of the dyebath are necessary. The fastness of the dyed colours to light, milling and acid satisfy the highest requirements.

*Alizarin Cyanine*, *Anthracene Blue* and *Brilliant Alizarin Blue* were discovered later than the above-mentioned alizarin blues, and, owing to their greater solubility and other advantages, they have largely replaced them as substitutes for indigo. They are dyed on chromium-mordanted wool, silk or cotton, and yield dark purplish or greenish blues, according to the particular brand employed. The fastness of the dyed colours to light, and general durability, are very satisfactory, but in fastness to milling and acids they are to some extent inferior to alizarin blue.

*Celestine Blue* and *Chrome Blue* dye purplish blue and bright blue respectively, and are dyed in the ordinary way upon a chromium mordant. The colours they yield are inferior to the Alizarin Colours in fastness to light, but on account of their clear shades they are often used for brightening other colours.

*Brilliant Alizarin Cyanine*, *Alizarin Viridine* and *Alizarin Saphirole* are true Alizarin Colours, and possess the same fastness to light as other colours of this class. Unlike most of the Alizarin Colours, they are capable of dyeing wool satisfactorily without the aid of a metallic mordant—namely, with the addition of sulphuric acid to the dyebath, in the same manner as the Acid Colours. If necessary, the dyed colours may be treated with bichromate of potash. The colours thus produced are very fast to light and very level, hence these dyestuffs are valuable in the production of the most delicate compound shades, such as drabs, slates, greys, &c., which are desired to be fast to light. *Alizarin saphirole* dyes clear blue, the colour produced being much more brilliant even than those of brilliant alizarin cyanine.

*Gallein*, *Gallocyanine*, and especially *Chrome Violet*, dye somewhat bright purple shades, and are hence frequently employed for brightening other colours, but they are only moderately fast to light. They are applied in the usual manner on a chromium mordant.

*Anthracene Brown* is largely employed in the production of compound shades. It dyes a dark, somewhat reddish, brown on chromium mordant, the colour being very even and extremely fast to light.

*Alizarin Black* is dyed on chromium mordant in the same manner as alizarin, and is used as a self-colour or in combination with other Alizarin Colours.

*Diamond Black* is very useful for dyeing good blacks on wool, fast to light and acids. The wool is first dyed with the addition of acetic and finally sulphuric acid. When the dyebath is exhausted,

bichromate of potash (2%) is added, and boiling is continued for half an hour longer.

The *erio chrome colours* (black, brown, red, &c.) are applied in wool dyeing like diamond black.

*Chromotrope*, of which there are several brands, is an Acid Colour which is applied to wool in an acid bath in the usual manner. The red or purple colours thus obtained are saddened in the same bath with bichromate of potash and changed into black, the colouring matter being oxidized and simultaneously combined with chromium.

MISCELLANEOUS COLOURS.—Under this head there may be arranged a few dyestuffs which, although capable of inclusion under one or other of the foregoing groups, it is more convenient to treat of separately. Indigo, Aniline Black and Catechu, for example, might be placed in the class of Developed Colours, since they are all developed on the fibre, and indeed by the same method, namely, by oxidation.

*Indigo* is one of our most important blue dyestuffs, which has been employed from the earliest times. Indigo, being insoluble in water, would be of no use in dyeing if it were not capable of being rendered soluble. This is effected in two ways, corresponding to which there are two methods of dyeing with indigo. One method consists in dissolving the indigo in very strong sulphuric acid, whereby it is converted into indigotin-disulphonic acid (Indigo Extract), which is readily soluble in water. This substance belongs to the group of Acid Colours; hence it is applied to the animal fibres, wool and silk, by boiling in a solution of the colouring matter slightly acidified with sulphuric acid. The second and most important method is based on the fact that under the influence of reducing agents (*i.e.* substances capable of yielding nascent hydrogen) indigo blue is changed into indigo white, which is soluble in alkali, the solution thus obtained being called a "vat." If textile materials are steeped in a clear yellow solution of the reduced indigo and then exposed to air, the indigo white absorbed by the fibre is oxidized and reconverted into indigo blue within and upon the fibre, which thus becomes dyed blue; this is the so-called "indigo-vat" method of dyeing. Comparing the two methods, the "indigo-extract" method is only applicable to the animal fibres, and although it gives brighter colours, they are fugitive to light and are decolorized by washing with alkaline solutions; the "vat method" is applicable to all fibres, and gives somewhat dull blues, which are very fast to light, washing, &c.

Cotton is dyed by means of the "*lime and copperas vat*," the "*zinc powder vat*," or the "*hydrosulphite vat*." In the first-mentioned vat the ingredients are quicklime, ferrous sulphate and finely ground indigo; the lime decomposes the ferrous sulphate and precipitates ferrous hydrate; this quickly reduces the indigo to indigo white, which dissolves in the excess of lime present. The ingredients of the zinc powder vat are zinc powder, lime and indigo; in the presence of the lime and indigo the zinc takes up oxygen from the water, liberating the hydrogen necessary to reduce the indigo, as in the previous vat. The constituents of the hydrosulphite vat are hydrosulphite of soda, lime and indigo. The requisite hydrosulphite of soda is prepared by allowing zinc powder (13 lb) to act upon a cold concentrated solution of bisulphite of soda (17 gallons of sp. gr. 1.225), taking care to avoid, as much as possible, access of air and any heating of the mixture, to prevent decomposition. The solution thus obtained is thoroughly neutralized by the addition of lime; and after settling, the clear liquor is used for the vat, along with indigo and lime. Here again the hydrosulphite takes up oxygen from the water and liberates the necessary hydrogen. It is found convenient to prepare, in the first instance, a very concentrated standard of reduced indigo, and to add as much of this to the dye-vat as may be required, along with lime and a little hydrosulphite of soda. The advantages of this vat are that it is easily prepared and that there is very little sediment; moreover, it can be employed in dyeing wool, as well as cotton, and it is now very generally in use. The vat usually employed for dyeing wool is the so-called "woad vat," which differs from the foregoing in that the hydrogen necessary to reduce the indigo and bring it into solution is furnished, not by the action of chemical agents, but by means of fermentation. The ingredients of the woad vat are indigo, woad, bran, madder and lime. The woad here employed is prepared by grinding the leaves of the woad plant (*Isatis tinctoria*) to a paste, which is allowed to ferment and then partially dried. It serves as the ferment to excite lactic and butyric fermentation with the aid of the bran and madder, the necessary hydrogen being thus evolved. Excessive fermentation is avoided by making timely additions of lime; sluggish fermentation is accelerated by additions of bran and slightly raising the temperature. When the reduction and complete solution of the indigo is effected, the vat is allowed to settle, and the woollen material is immersed and moved about in the clear liquor for half an hour to two hours, according to the shade required, then squeezed and exposed to the air in order to develop the blue colour on the fibre.

*Thioindigo red* is an artificial colouring matter belonging to the indigo series and comes into the market in the form of a paste. It is used in dyeing in exactly the same way as indigo, yielding shades which range from a somewhat dull pink to a full claret shade of red. The colours obtained are remarkable for their fastness.

*Indanthrene*. This colouring matter, which is also sold as a paste,

is an anthracene derivative, being formed by the action of caustic potash on  $\beta$ -amidoanthraquinone. It is reduced by hydrosulphite of soda yielding a blue vat, in which cotton and other vegetable fibres are dyed in the same way as in the indigo vat. Since a fair amount of caustic soda is necessary for the setting of the vat, the dyestuff is not suitable for animal fibres. Indanthrene yields on cotton reddish shades of blue which are extremely fast to all external influences; in fact the colour is so fast that when once fixed on cotton it cannot be removed again from the fibre by any known means.

Other vat colours belonging to this series, which are similarly applied, are flavanthrene (yellow), viridanthrene (green), fuscianthrene (grey-brown), violanthrene (dull violet) and melanthrene (grey to black). The *algol colours* resemble the indanthrene colours in their properties and application.

*Aniline Black* differs from other dyes in that it is not sold as a ready-made dyestuff, but is produced *in situ* upon the fibre by the oxidation of aniline. It is chiefly used for cotton, also for silk and cotton-silk union fabrics, but seldom or not at all for wool. Properly applied, this colour is one of the most permanent to light and other influences with which we are acquainted. One method of dyeing cotton is to work the material for about two hours in a cold solution containing aniline (10 parts), hydrochloric acid (20 parts), bichromate of potash (20 parts), sulphuric acid (20 parts), and ferrous sulphate (10 parts). The ferrous sulphate here employed is oxidized by the chromic acid to a ferric salt, which serves as a carrier of oxygen to the aniline. This method of dyeing is easily carried out, and it gives a good black; but since much of the colouring matter is precipitated on the fibre superficially as well as in the bath itself, the colour has the defect of rubbing off. Another method is to impregnate the cotton with a solution containing aniline hydrochloride (35 parts), neutralized with addition of a little aniline oil, sodium chlorate (10 parts), ammonium chloride (10 parts). Another mixture is 1.8 part aniline salt, 12 parts potassium ferrocyanide, 200 parts water, 3.5 parts potassium chlorate dissolved in water. After squeezing, the material is passed through a special oxidation chamber, the air of which is heated to about 50° C. and also supplied with moisture. This oxidizing or ageing is continuous, the material passing into the chamber at one end in a colourless condition, and after about 20 minutes passing out again with the black fully developed, a final treatment with hot chromic acid solution and soaping being necessary to complete the process. In this method, employing the first-mentioned solution, chlorate of copper is formed, and this being a very unstable compound, readily decomposes, and the aniline is oxidized by the liberated chlor-oxygen compounds. The presence in the mixture of a metallic salt is very important in aiding the development of the black, and for this purpose salts of vanadium, cerium and copper have proved to be specially useful. The chemistry of aniline black is still incomplete, but it would appear that there are several oxidation products of aniline. The first product is so-called emeraldine, a dark green substance of the nature of a salt, which by treatment with alkali yields a dark blue base called azurine. The further oxidation of emeraldine yields nigraniline, also a dark green salt, but the free base of which has a violet black colour. The latter becomes greenish under the influence of acids, especially sulphuric acid, and this explains the defect known as "greening" which is developed in ordinary aniline blacks during exposure to air. By a supplementary oxidation with chromic acid such a black is rendered ungreenable, the nigraniline being probably changed into the more stable chromate of nigraniline.

*Catechu* is a valuable brown dyestuff, obtained from various species of *Acacia*, *Areca* and *Uncaria* growing in India. The wood, leaves and fruit of these plants are extracted with boiling water; the decoction is then evaporated to dryness or to a pasty consistency. Catechu is largely used by the cotton dyer for the production of brown, drab and similar colours. It is seldom employed for wool. Cotton is usually dyed by boiling it for about one hour in a decoction of catechu (100%) containing copper sulphate (5%). After squeezing, the material is boiled for about fifteen minutes in a solution of bichromate of potash ( $\frac{1}{4}$  oz. per gal.), then washed and dried. By repeating the operations two or three times deeper shades are obtained. During the boiling with catechu the cotton attracts the active principles catechin and catechu-tannic acid, but it thus acquires only a pale brown colour; in the bichromate of potash, however, these are oxidized to form insoluble japonic acid, which permeates the fibre, and a deep brown colour is thus developed. Catechu browns are fast to a variety of influences, *e.g.* washing, alkalis, acids, &c., but less so to light. Catechu has been recently much employed, in conjunction with copper sulphate, for dyeing the so-called khaki-brown on woollen material for military clothing. On silk, catechu is much used for weighting purposes in dyeing black.

MINERAL COLOURS.—Those include Chrome Yellow, Iron Buff, Prussian Blue and Manganese Brown.

*Chrome Yellow* is only useful in cotton-dyeing as a self-colour, or for conversion into chrome orange, or, in conjunction with indigo, for the production of fast green colours. The cotton is first impregnated with a solution of lead acetate or nitrate, squeezed, and then passed through a solution of sodium sulphate or lime water to fix the lead on the fibre as sulphate or oxide of lead. The



material is then passed through a solution of bichromate of potash. The colour is changed to a rich orange by a short, rapid passage through boiling milk of lime, and at once washing with water, a basic chromate of lead being thus produced. The colour is fast to light, but has the defect of being blackened by sulphuretted hydrogen.

*Iron Buff* is produced by impregnating the cotton with a solution of ferrous sulphate, squeezing, passing into sodium hydrate or carbonate solution, and finally exposing to air, or passing through a dilute solution of bleaching powder. The colour obtained, which is virtually oxide of iron, or iron-rust, is fast to light and washing, but is readily removed by acids.

*Prussian Blue* is applicable to wool, cotton and silk, but since the introduction of coal-tar blues its employment has been very much restricted. The colour is obtained on cotton by first dyeing an iron buff, according to the method just described, and then passing the dyed cotton into an acidified solution of potassium ferrocyanide, when the blue is at once developed. A similar method is employed for silk. Wool is dyed by heating it in a solution containing potassium ferricyanide and sulphuric acid. The colour is developed gradually as the temperature rises; it may be rendered brighter by the addition of stannous chloride. On wool and silk Prussian blue is very fast to light, but alkalis turn it brown (ferric oxide).

*Manganese brown or bronze* is applied in wool, silk and cotton dyeing. The animal fibres are readily dyed by boiling with a solution of potassium permanganate, which, being at first absorbed by the fibre, is readily reduced to insoluble brown manganic hydrate. Since caustic potash is generated from the permanganate and is liable to act detrimentally on the fibre, it is advisable to add some magnesium sulphate to the permanganate bath in order to counteract this effect. Imitation furs are dyed in this manner on wool-plush, the tips or other parts of the fibres being bleached by the application of sulphurous acid. Cotton is dyed by first impregnating it with a solution of manganous chloride, then dyeing and passing into a hot solution of caustic soda. There is thus precipitated on the fibre manganous hydrate, which by a short passage into a cold dilute solution of bleaching powder is oxidized and converted into the brown manganic hydrate. This manganese bronze or brown colour is very susceptible to, and readily bleached by, reducing agents; hence when exposed to the action of an atmosphere in which gas is freely burnt, the colour is liable to be discharged, especially where the fabric is most exposed. In other respects manganese bronze is a very fast colour.

*Dyeing on a large Scale.*—It is not possible to give here more than a bare outline of the methods which are used on the large scale for dyeing textile fibres, yarns and fabrics. In principle, dyeing is effected by allowing an aqueous<sup>1</sup> solution of the dyestuff, with or without additions (alkalis, acids, salts, &c.), to act, usually at an elevated temperature, on the material to be dyed. During the process it is necessary, in order to ensure the uniform distribution of the dyestuff in the material, that the latter should either be moved more or less continuously in the dye liquor or that the dye liquor should be circulated through the material. The former mode of operation is in general use for hank, warp and piece dyeing, but for textile fibres in the loose condition or in the form of "slubbing," "sliver" or "cops" (see SPINNING) the latter method has, in consequence of the introduction of improved machinery, come more and more into vogue within recent years.

*Loose Material.*—Cotton and wool are frequently dyed in the loose state, *i.e.* before being subjected to any mechanical treatment. The simplest method of effecting this is to treat the material in open vessels (boilers) which can be heated either by means of steam or direct fire. Since, however, a certain amount of felting or matting of the fibres cannot be avoided, it is frequently found to be more advantageous to effect these treatments in specially constructed apparatus in which the dye liquors are circulated through the material.

*Yarn.*—Yarn may be dyed either in the hank, in the warp or in the cop, *i.e.* in the form in which the yarn leaves the spinning frame. The dyeing in the *hank* is carried out in rectangular dye-vats constructed of wood or stone like that shown in fig. 1, in which the hanks are suspended from smooth wooden poles or rods resting on the sides, and are thus immersed almost entirely in the dye liquor. The heating of the vat is effected either by means of live steam, *i.e.* by blowing steam into the dye solution from a perforated pipe which runs along the bottom of the vat,

or by means of a steam coil similarly situated. In order to expose the hanks as uniformly as possible to the action of the dye liquor, they are turned by hand at regular intervals until the operation is finished. Washing off is effected in the same or in a similar vessel, after which excess of water is removed by wringing by hand, through squeezing rollers or, what is generally preferred, in a hydro-extractor (centrifugal machine). The drying of the dyed and washed yarn is generally effected by suspending it

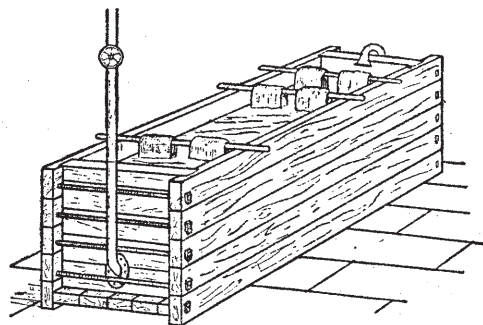


FIG. 1.—Dye-vat for Yarn.

on poles in steam-heated drying chambers. Yarn in the *warp* is dyed in vats or "boxes" like that shown in fig. 2, through which it is caused to pass continuously. The warps to be dyed pass slowly up and down over the loose rollers in the first box B, then through squeezing rollers S into the next, and the same thing occurs in the second (also third and fourth in a four-box machine) box A, whence they are delivered through a second pair of squeezing rollers S<sub>1</sub> into the wagon W. The boxes may contain the same or different liquors, according to the nature of the dyestuff employed. Washing is done in the same machine, while drying is effected on a cylinder drying machine like that shown in figs. 8 and 9 of BLEACHING. Latterly, machines have been introduced for dyeing warps on the beam, the dye liquor being caused to circulate through the material, and the system appears to be meeting with considerable success. Large quantities of yarn, especially cotton, are now dyed in the cop. When the dyed yarn is to be used as weft the main advantage of this method is at once apparent, inasmuch as the labour, time and waste of material incurred by reeling into hanks and then winding back into the compact form so as to fit into the shuttle are avoided. On the other hand the number of fast dyestuffs suitable for cop dyeing is very limited. In the original cop-dyeing machine constructed by Graemiger a thin tapering perforated metallic tube is inserted in the hollow of each cop. The cops are then attached to a perforated disk (which con-

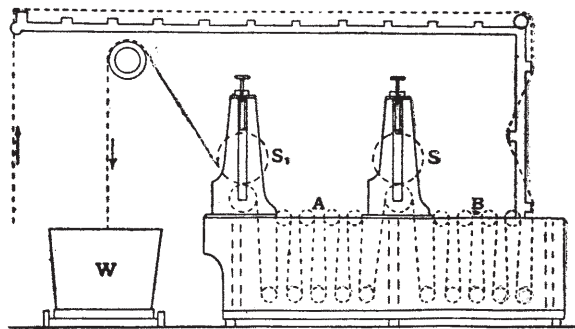


FIG. 2.

stitutes the lid of a chamber or box) by inserting the protruding ends of the tubes into the perforations. The chamber is now immersed in the dye-bath and the hot liquor is drawn through the cops by means of a centrifugal pump and returned continuously to the dye-bath. This principle, which is known as the skewer or spindle system, is the one on which most modern cop-dyeing machines are based. In the so-called "compact" system of cop dyeing the cops are packed as closely as possible in a box, the top and bottom (or the two opposite sides) of which are

<sup>1</sup> The term "dry dyeing," which is carried out only to a very limited extent, relates to the dyeing of fabrics with the dyestuff dissolved in liquids other than water, *e.g.* benzene, alcohol, &c.

perforated, the interstices between the cops being filled up with loose cotton, ground cork or sand. The dye liquor is then drawn by suction or forced by pressure through the box, thus permeating and dyeing the cops.

*Pieces.*—Plain shades are usually dyed in the piece, this being the most economical and at the same time the most expeditious means of obtaining the desired effect. The dyeing of piece goods may be effected by running them through the dye liquor either at full breadth or in rope form. The machine in most common use for the first method is the Lancashire "jigger," which is simple in principle and is shown in section in fig. 3. It consists essentially of a dye-vessel constructed of wood or cast iron and containing loose guide rollers,  $r$  and  $r$ , at the top and bottom. By coupling up the roller B with the driving gear

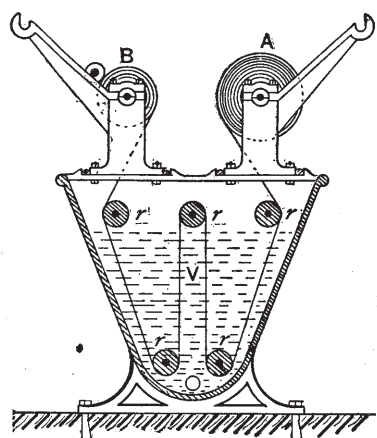


FIG. 3.—Dye-jigger.

on A are drawn through the dye liquor and rolled on to B. A band brake (not shown in the figure) applied to the axis of A gives the pieces the required amount of tension in passing through the dye-bath. As soon as the whole of the pieces have passed through in this way from A to B, the machine is reversed, and roller A draws them back again through the bath in a similar way on to roller A. This alternating process goes on until the dyeing is finished, when the goods are washed off, squeezed and dried. The jigger is especially useful in cotton piece dyeing, one great advantage being that it is suited for what is known as a "short bath," *i.e.* a bath containing a minimum amount of dye liquor, this being of great importance in the application of dyestuffs which do not exhaust well, like the direct colours and the sulphide colours. The padding machine is similar in principle to the jigger, the pieces running over loose guide rollers through the mordant or dye solution contained in a trough of suitable shape and size, but on leaving the machine they pass through a

pair of squeezing rollers which uniformly express the excess of liquor and cause it to be returned to the bath. The padding machine is used more for preparing (mordanting, &c.) than for dyeing.

For the dyeing of pieces in rope form a so-called "dye-beck" is used, which is a machine of larger dimensions than the jigger. Across the dye-bath is attached a winch W (see fig. 4), by means of which the pieces, sewn together at the ends so as to form an end-

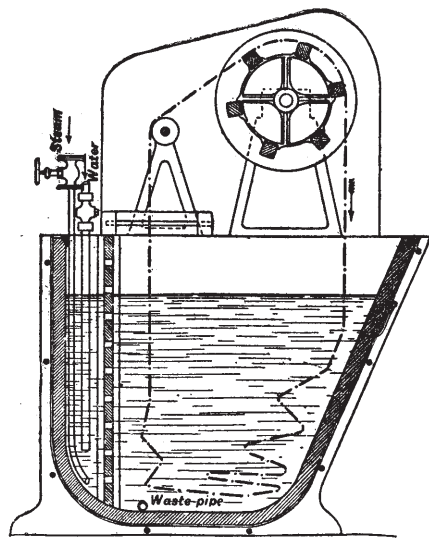


FIG. 4.—Dye-vat for Piece Goods.

less band, are caused to circulate through the machine, being drawn up on the front side of the machine and allowed to drop back into the dye liquor on the other. This form of machine is particularly suited for the mordanting and dyeing of heavy goods. Washing off may be done in the same machine.

The drying of piece goods is done on steam-heated cylinders like those used for the drying of bleached goods (see BLEACHING).

The operations which precede dyeing vary according to the material to be dyed and the effects which it is desired to produce. Loose wool, woollen and worsted yarn and piece goods of the same material are almost invariably scoured (see BLEACHING) before dyeing in order to remove the oily or greasy impurities which would otherwise interfere with the penetration of the dye solution. Silk is subjected to the process of discharging or boiling off (see BLEACHING) in order to remove the silk gum or sericine. Cotton which is to be dyed in dark shades does not require any preparatory treatment, but for light or very bright shades it is bleached before dyeing. Wool and silk are seldom bleached before dyeing. Cotton, wool and union (cotton warp and worsted weft) fabrics are frequently singed (see BLEACHING) before dyeing. Worsted yarn, especially two-fold yarn, is very liable to curl and become entangled when scoured, and in order to avoid this it is necessary to stretch and "set" it. To this end it is stretched tight on a specially constructed frame, placed in boiling water, and then cooled. Similarly, union fabrics are liable to "cockle" when wetted, and although this defect may be put right in finishing, spots of water or raindrops will give an uneven appearance of a permanent character to the goods. To avoid this, the pieces are subjected previous to dyeing to the so-called "crabbing" process, in which they are drawn under great tension through boiling water and wound on to perforated hollow cylinders. Steam is then blown through the goods and they are allowed to cool.

With respect to the question of colour, we meet with two kinds of substances in nature, those which possess colour and those which do not. Why this difference? The physicist says the former are bodies which reflect all the coloured rays of the spectrum composing white light—if opaque, they appear white; if transparent, they are colourless. The latter are bodies which absorb some of the spectrum rays only, reflecting the remainder, and these together produce the impression of colour. A black substance is one which absorbs all the spectrum rays. The fundamental reason, however, of this difference of action on the part of substances towards light remains still unknown. All substances which possess colour are not necessarily dyestuffs, and the question may be again asked, Why? It is a remarkable circumstance that most of the dyestuffs at present employed occur among the so-called aromatic or benzene compounds derived from coal-tar, and a careful study of these has furnished a general explanation of the point in question, which briefly is, that the dyeing property of a substance depends upon its chemical constitution. Speaking generally, those colouring matters which have the simplest constitution are yellow, and as the molecular weight increases their colour passes into orange, red, violet and blue. In recent years chemists have begun to regard the constitution of nearly all dyestuffs as similar to that of Quinone, and some even believe that all coloured organic compounds have a quinonoid structure. According to O. N. Witt, a colourless hydrocarbon, *e.g.* benzene, becomes coloured by the introduction of one or more special groups of atoms, which he terms the colour-bearing or *chromophorous groups*, *e.g.*  $\text{NO}_2$ ,  $-\text{N}:\text{N}-$ , &c. Benzene, for example, is colourless, whereas nitro-benzene and azo-benzene are yellow. Such compounds containing chromophorous groups are termed chromogens, because, although not dyestuffs themselves, they are capable of generating such by the further introduction of salt-forming atomic groups, *e.g.* OH,  $\text{NH}_2$ . These Witt terms *auxochromous groups*. In this way the chromogen *tri-nitro-benzene*,  $\text{C}_6\text{H}_3(\text{NO}_2)_3$ , becomes the dyestuff *tri-nitro-phenol* (picric acid),  $\text{C}_6\text{H}_2(\text{NO}_2)_3(\text{OH})$ , and the chromogen *azo-benzene*,  $\text{C}_6\text{H}_5:\text{N}:\text{N}:\text{C}_6\text{H}_5$ , is changed into the dyestuff *amido-azo-benzene* (Fast Yellow),  $\text{C}_6\text{H}_5:\text{N}:\text{N}:\text{C}_6\text{H}_4(\text{NH}_2)$ . These two dyestuffs are typical of a large number which possess either an acid or a basic character according as they contain hydroxyl (OH) or amido ( $\text{NH}_2$ ) groups, and correspond to the Acid Colours and Basic Colours to which reference has already been made. Other important atomic groups which frequently occur, in addition to the above, are the carboxyl ( $\text{COOH}$ ) and the sulphonic acid ( $\text{HSO}_3$ ) groups; these either increase the solubility of the

*Theory of dyeing.*

colouring matter or assist in causing it to be attracted by the fibre, &c. In many cases the free colour-acid or free colour-base has little colour, this being only developed in the salt. The free base rosaniline, for example, is colourless, whereas the salt magenta (rosaniline hydrochloride) has a deep crimson colour in solution. The free acid Alizarin is orange, while its alumina-salt is bright red. It may be here stated that the scientific classification of colouring matters into Nitro-colours, Azo-colours, &c., already alluded to, is based on their chemical constitution, or the chromophorous groups they contain, whereas the classification according to their mode of application is dependent upon the character and arrangement of the auxochromous groups. The question of the mordant-dyeing property of certain colouring matters containing (OH) and (COOH) groups has already been explained under the head of *Artificial Mordant Colours*.

The peculiar property characteristic of dyestuffs, as distinguished from mere colouring matters, namely, that of being readily attracted by the textile fibres, notably the animal fibres, appears then to be due to their more or less marked acid or basic character. Intimately connected with this is the fact that these fibres also exhibit partly basic and partly acid characters, due to the presence of carboxyl and amido groups. The behaviour of magenta is typical of the Basic Colours. As already indicated, rosaniline, the base of magenta, is colourless, and only becomes coloured by its union with an acid, and yet wool and silk can be as readily dyed with the colourless rosaniline (base) as with the magenta (salt). The explanation is that the base rosaniline has united with the fibre, which here plays the part of an acid, to form a coloured salt. It has also been proved that in dyeing the animal fibres with magenta (rosaniline hydrochloride), the fibre unites with the rosaniline only, and liberates the hydrochloric acid. Further, magenta will not dye cotton unless the fibre is previously prepared, e.g. with the mordant tannic acid, with which the base rosaniline unites to form an insoluble salt. In dyeing wool it is the fibre itself which acts as the mordant. In the case of the Acid Colours the explanation is similar. In many of these the free colour-acid has quite a different colour from that of the alkali-salt, and yet on dyeing wool or silk with the free colour-acid, the fibre exhibits the colour of the alkali-salt and not of the colour-acid. In this case the fibre evidently plays the part of a base. Another fact in favour of the view that the union between fibre and colouring matter is of a chemical nature, is that by altering the chemical constitution of the fibre its dyeing properties are also altered; oxycellulose and nitrocellulose, for example, have a greater attraction for Basic Colours than cellulose. Such facts and considerations as these have helped to establish the view that in the case of dyeing animal fibres with many colouring matters the operation is a *chemical* process, and not merely a mechanical absorption of the dyestuff. A similar explanation does not suffice, however, in the case of dyeing cotton with the Direct Colours. These are attracted by cotton from their solutions as alkali salts, apparently without decomposition. The affinity existing between the fibre and colouring matter is somewhat feeble, for the latter can be removed from the dyed fibre by merely boiling with water. The depth of colour obtained in dyeing varies with the concentration of the colour solution, or with the amount of some neutral salt, e.g. sodium chloride, added as an assistant to the dye-bath; moreover, the dye-bath is not exhausted. The colouring matter is submitted to the action of two forces, the solvent power of the water and the affinity of the fibre, and divides itself between the fibre and the water. After dyeing for some time, a state of equilibrium is attained in which the colouring matter is divided between the fibre and the water in a given ratio, and prolonged dyeing does not intensify the dyed colour.

Some investigators hold the view that in some cases the fibres exert a purely physical attraction towards colouring matters, and that the latter are held in an unchanged state by the fibre. The phenomenon is regarded as one of purely mechanical surface-attraction, and is compared with that exercised by animal charcoal when employed in decolorizing a solution of some colouring matter. Some consider such direct dyeing as mere diffusion of

the colouring matter into the fibre, and others that the colouring matter is in a state of "solid solution" in the fibre, similar to the solution of a metallic oxide in coloured glass. According to this latter view, the cause of the dyeing of textile fibres is similar to the attraction or solvent action exerted by ether when it withdraws colouring matter from an aqueous solution by agitation. Latterly the view has been advanced that dyeing is due to precipitation of the colloid dyestuffs by the colloid substance of the fibre.

In the case of colours which are dyed on mordant, the question is merely transferred to the nature of the attraction which exists between the fibre and the mordant, for it has been conclusively established that the union between the colouring matter and the mordant is essentially chemical in character.

From our present knowledge it will be seen that we are unable to give a final answer to the question of whether the dyeing process is to be regarded as a chemical or a mechanical process. There are arguments and facts which favour both views; but in the case of wool and silk dyeing, the prevailing opinion in most cases is in favour of the chemical theory, whereas in cotton-dyeing, the mechanical theory is widely accepted. Probably no single theory can explain satisfactorily the fundamental cause of attraction in all cases of dyeing, and further investigation is needed to answer fully this very difficult and abstruse question.

The poisonous nature or otherwise of the coal-tar dyes has been frequently discussed, and the popular opinion, no doubt dating from the time when magenta and its derivatives were contaminated with arsenic, seems to be that they are for the most part really poisonous, and ought to be avoided for colouring materials worn next the skin, for articles of food, &c. It is satisfactory to know that most of the colours are not poisonous, but some few are—namely, Picric acid, Victoria Orange, Aurantia, Coralline, Metanil Yellow, Orange II. and Safranine. Many coal-tar colours have, indeed, been recommended as antiseptics or as medicinal remedies, e.g. Methyl Violet, Auramine and Methylene Blue, because of their special physiological action. In histology and bacteriology many coal-tar colours have rendered excellent service in staining microscopic preparations, and have enabled the investigator to detect differences of structure, &c., previously unsuspected. In photography many of the more fugitive colouring matters, e.g. Cyanine, Eosine, Quinoline Red, &c., are employed in the manufacture of ortho-chromatic plates, by means of which the colours of natural objects can be photographed in the same degrees of light and shade as they appear to the eye—blue, for example, appearing a darker grey, yellow, a lighter grey, in the printed photograph.

Since the year 1856, in which the first coal-tar colour, mauve, was discovered, the art of dyeing has made enormous advances, mainly in consequence of the continued introduction of coal-tar colours having the most varied properties and suitable for nearly every requirement. The old idea that the vegetable dyestuffs are superior in fastness to light is gradually being given up, and, if one may judge from the past, it seems evident that in the future there will come a time when all our dyestuffs will be prepared by artificial means.

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(J. J. H.; E. K.)