DYEING (O. Eng. dægian, dæk; Mod. Eng. dye), 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
probaby 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 un-
civilized 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 sketch.

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 Phoenicia and Egypt,
with which countries commercial intercourse, by way of the
Persian and Arabian Gulls, 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 1500 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 Phoenician 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 succeed-
ning 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 redis-
covered 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 Marigela 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 incorpo-
rated 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 oper-
ations of dyeing, by publishing a code of instructions for the use of
the woolen 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, Heliot, Macquer, Berthollet,
Roard and Chevreul (1780-1823) all rendered excellent service to
the art, by investigating the chemical principles of dyeing, by
publishing accounts of the various processes in vogue, by examin-
ing 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 dis-
appeared, 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
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 the following groups:

(1) Nitro Colours.
(2) Azo Colours—Including Aminido- and Azo-derivatives.
(3) Tetrazo and Polyazo Colours.
(4) Hydrazo Colours.
(5) Oxy-quinone Colours, including Quinone-oxide Colours.
(6) Diphenylmethane and Triphenylmethane Colours, including Rossanilin, Rosolic acid and Phthalein Colours.
(7) Quinone-imide Colours, including Indamine, Indophenol, Thiazine, Thionazo, Oxazone, Oxazine, Azine, Induline, Quinoxaline and Fluorindine Colours.

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 a very close relationship between some of these groups, for many colours are applicable by more than one of these methods, 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 acidic 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 (NO₂) or sulphonic acid (HSO₃⁻) groups. According to their origin and constitution they may be distinguished into nitro-compounds and nitro-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 lactic 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 dyebath with the amount of dyestuff necessary to give the required colour, say from 5 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 woolen material is then...
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 2 to 1 hour; after boiling for 2 to 3 hours longer, the operation is complete, and the material is washed and dried.

In commercial practice, the operations of dyeing an even colour, i.e. free from such irregularities as cloudiness, streaks, &c., which may be due to the quality of the materials, the manner of dyeing them, or the action of the alkali, are very exacting. Matter 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. For instance, silk is employed to form a special class of dyestuffs and 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, but the equal, direct or indirect, fixation 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 amyl 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, in the 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 material and the diffusion of other substances occurring as 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 colour is fixed upon it. The fibre is then washed and the excess of 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. While 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 should be employed.

The properties of the dyestuffs obtained with the acid colours are extremely varied. Many are fugitive to light; on the other hand, many are very fast, some of the most brilliant being very fast 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. Silk and wool are dyed in a neutral bath. In any addition, the material not requiring any previous preparation. During the dyeing operation the material fibres appear to play the part of an acid, for they decompose the colouring matter and unite with the acetic acid to form a special class of dyestuffs, and the union of 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 darker and stronger tone of colour, while in the case of silk 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) and finally, also slightly acetic acid. A full colour is secured by a full colour use 2 or 3% colouring matter, enter the wool at a low temperature, heat gradually to the boiling point in the course of 1 hour, and continue dyeing for 1 hour. Owing to the slight solubility of many basic or moderately water-soluble substances, care is necessary in 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 dye 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 through a bath containing 2 or 3% of tannic acid (e.g. Chrome Brown, Chromogen, Alizarin Yellow, &c.), 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 is not liberated by water, and to insure its permanence. 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 tannin-alkaloid compound, 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 deconcentration of sumach, myrabolans, or other tannin matter, and to 3% tartar emetic. After mordanting, the cotton is worked in a bath containing 2 or 3% of the mordant for 1 hour in the cold or at 60° C. for 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.

Linseed 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 one vegetable dye, namely, the acetic acid, 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, pyrione red, rhodine red, rosazin, indiline scarlet.

Orange.—Chrysolein, phosphine, acridine orange, tannin orange.

Yellow.—Auramine, benzoflavine, thiophanon T, acridine yellow, homophosphine, rhodine yellow.

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

Blue.—Methylene blue, new methylene blue, toluidine blue, thionine blue, indamine blue, Victoria blue, light blue, Nile blue, ultramarine blue, marine blue, blues, Capri blue, indazine, metaphenylene blue, paraphenylene blue, toluidine blue, indigine, indol blue, diphene blue, setolane, scopetane, setopane, Helvetia blue.

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

Brown.—Bismarck brown.

Black.—Diazine black.

Grey.—Methylene grey, nigrosin, new grey.

Direct Colours.—The characteristic feature of the dyestuffs belonging to this class is the fact that they are fast “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.

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 sulfonlated tetrasulpho-
dyes obtained by diazotizing certain dianium compounds, e.g., benzyl-
dimido-stilbene, &c., and unifying 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 large number of dyes have been invented which yield a large
variety of colour. The method of dying of cotton consists in merely
boiling the material in a solution of the dyestuff, when the cotton
albedo 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 dye is exhausted at about 10% of the dye liquor, and imperfect
dyeing results. With many dyestuffs it is preferable to use
½ to 1 oz. soap instead of soda. On cotton the dyed colours
are usually not very fast to light, and some are sensitive to alkali
or 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 (½ hour) after-treatment with a boiling solution of
sodium carbonate (1%), with or without the addition of bicromate 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 dyestuffs are usually very fast to light and washing,
milling and light; some are very fast even to light—e.g., Diamine
fast red, chrysophene, Hessian yellow, &c. Many of the Direct
Colours are very useful for dying plain shades on union fabrics
coverings, and are very cheap, cotton, and silk. Owing to the facility of their application, they are also very suitable
for use as household dyes, especially for cotton goods.

Dyeing.—The dyestuffs belonging to this class, notably Turmeric,
saffron, annatto and safflower, dye the fibres yellow colours which
are fugitive to light, and are now of little importance. Tur-
meric is the underground stem or tuber of Curcuma tinctoria, a
plant growing 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 Spain. It dyes cotton, wool and silk in an alkaline or acid
solution, yielding a bright orange-yellow. Annatto is the pulp 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 acid bath an orange colour, which
is deepened and fixed by acids. Annatto is a very important
dye for the East Indies, Egypt and southern Europe. Cotton
is dyed a bright pink colour by working it in cold alkali. (See also
the following extracts.)

DYEING.—The Direct dyes which are derived from coal-tar products
are very numerous; they are highly valued as they are cheap,
and are of very great importance among the dyestuffs. The
following list includes the principal coal-tar dyes:

Red.—Congo red, bright Congo, benzopurpurine, brilliant
purpurine, carmine, dianium, Congo red, indigo, rosinarine,
salmon red, erica, Titan pink, St Denis red, Congo red,
naphthol red, Congo rubine, aceto-purpurine, dianium red,
thiavanine, brilliant carmine, dianium fast scarlet, dianium
fast red, thiavanine red, dianium red, rosaline, Dianium
rose, Dianium red, rosophthalein.

Orange.—Congo orange, benzo orange, tolulene orange, mikoado
orange, brilliant orange, Columbia orange, diamin orange,
pyramine orange, benzo fast orange.

Yellow.—Chrysamine, cresotin yellow, dianium yellow, carbolaz
yellow, chrysophene, Hessian yellow, curcumin yellow, thiazol
yellow, thioflavine S, orio1, mimosa yellow, Columbia yellow,
cotton yellow, chlorocarbocyanin, direct yellow, dianium fast yellow, dianium gold, sun yellow, stilbene yellow, chlorophene, oxyphene.

Green.—Benzo olive, Columbia green, benzo green, diamin green,
diamine green, oxamine green, eelgreen.

Blue.—Azo blue, benzopurpurine, benzopurpurine, azo-azureine,
diamine blue, benzo indigo blue, benzol blue, Chicago blue,
Columbia blue, Eric blue, Zambesi blue, benzo cyanine, Congo blue,
diphenyl blue, benzol chrome black blue, oxamine blue, diphenyl blue, dianinblue, diaminogene, benzo fast blue, diazo indigo blue, brilliant chloro blue.

Violet.—Hessian purple, Congo Corinth, heliotrope, Congo violet,
dianium violet, dianium violet, benzol violet, oxo violet, Zambesi
di Vine, Bordeaux, chlorazine lilac, diphenyl violet, triazo violet,
Columbia violet.

Black.—Bezo benzol, Congo brown, tolulene brown, diamin
brown, cotton brown, Hessian brown, brilliant black, indigo
catech brown, wool brown, Columbia brown, Zambesi brown,
benzo chrome brown, direct fast brown, direct bronze brown,
chrysophene violet, triazoil brown, tolulene brown, diamin brown,
Cromspall direct fast brown.

White.—Diamine black, Columbia black, Nyanza black, Tabora
black, Zambesi black, chromolin black, benzo black, benzo black,
direct blue black, Plut0 black, oxydiamine black, diamin
jet black, polyphenyl black, Union black, triazoil black, Titan black,
cotton black, oxamine black.

Grey.—Benzo grey, benzo black, azo mave, diaminogene, neutral
grey.

Salt 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 member of this group, and was obtained by neutralising a mixture
of sodium sulphate and a strong solution of sodium thiosulphate
and fine dust, &c. In recent years numerous other dyestuffs have
been added to the list, namely, grey, blue, green, brown, and especially black
dyestuffs. For the preparation of these the amido compounds of the
aromatic series to a similar treatment with yellow chrome sulphides
or sodium thiosulphate, and subsequent oxidation. The mode
of dyeing with these colours is based on the fact that they are soluble
in alkaline bath and not reduced in the cold, and if the solution
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
bicromate of soda, and 3 to 6%, acetic acid. A final washing
with water containing a little soda to remove acidity is advisable. The
salt colours are remarkable for their fastness to light, alkalis,
acids and washing, but unless proper care is exercised the cotton is
apt to become yellowed for some time.

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

Yellow.—Immediatly yellow, pyrogene yellow, sulphur yellow,
thiavanine yellow, oxidimone yellow.

Orange.—Eclipse phosphine, immediatly orange, pyrogene orange,
thion orange, thiavanine orange.

Green.—Pyrogene green, Italian green, eclipse green, pyrol green,
impermeable green, kattigene. indigo, pyrogene blue, sulphur blue, thinon blue, thiavanine blue.

Blue.—Kattigene violet, thiavanine heliotrope, thiavanine purple.

Brown.—Pyrogene brown, hellebore yellow, Cachou de Laval,
thiocatheine, kattigene black brown, eclipse brown, immediatly brown,
kattigene brown, diamin brown.

Black.—Pyrogene black.—Pyrone black, benzol black, immediate black,
epidine black, anthraquinone black, St Denis black, amidoazol
black, cross dye black, eclipse black, carbide black, thiavanine black,
sulphamine black, sulfogen black, pyrogene black, diamin black,
sulphamine black, thiavanine black, coloured black, flavine
black, thion black, thiavanine 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.
This is known as the so-called insoluble Azo Colours, Developed Directs, Benzol Nitro Colours.

(c) The Insoluble Azo Colours are produced as insoluble
coloured precipitates by adding a solution of a diazo compound
solution in water and the dye to an amido compound. The necessary
diazo compound is prepared by allowing a solution containing nitrous acid to act upon a solution
of a primary amonic acid. It is usually desirable to keep the
amido compound with ice, or at least with very cold water, as the diazo
compounds produced. The colour obtained varies according to the
particular diazo compound, as well as the amine or phenol
employed, β-naphthol being the most useful among the latter. The
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
compound. The most important of these colours is para-nitranilin
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 gms. β-naphthol, 20 gms.
cotton, 70 gms. water and 50 gms. nitrous acid in 1000 gms. (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 gms. para-nitranilin
are dissolved in 150 gms. 5% c.c. hydrochloric acid, and 1000 gms. of water. To the cold solution a solution of 10 gms. sodium nitrate
is added while stirring. The whole is then made up to 1200 c.c.,
then the cotton is introduced and before use 50 gms. sodium carbonate are added. This 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, soaked slightly, and finally rinsed
in water and then dried. The cotton is then fast to soap but not to light. If the para-nitranilin used in the foregoing
process is replaced by meta-nitranilin, a yellowish-orange
colour is obtained; with ε-naphthylamine, a claret-red; with amidoazol
and a browning agent, a brown with benzyl chloride; with
diaminamide, 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, also fast to light and to 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 primuline dye W, thus obtaining primuline yellow by dyeing cotton to light and of little practical value, but since the colouring matter is an amido base it can be diazotised in the fibre and then developed in solutions of phenols or amines, whereby azo dyes of various hues can be obtained, according to the amido base used.

The dyestuff 3-phenylazo-4-naphthol (Napscal) which is a red, is a diazotising substance for cotton. The dyestuff is boiled with cotton for 5 to 10 minutes in a cold solution of nitrous acid—i.e. a solution of nitrous acid per litre of water, slightly concentrated with sulphuric acid. The diazotised material should not be exposed to light, but at once washed in cold water and passed into the dyer.

The developing process consists in working the diazotised material for 1 hour in a cold solution of the phenol or amine, slightly heated, in a solution containing 2 to 3% of bichromate of potash on the weight of the wool employed. During this operation the wool at first becomes a yellow colour by reason of the bichromate of chromic chloride, so that the mordanted fibre has finally a pale olive-yellow tint. In thedyebath, 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 serves the same purpose as in the case of the wool on the wool to chromic hydrate already in the mordant bath, and the pale greenish mordanted wool is better adapted for dyeing with vanadium pentoxide, as these are susceptible to oxidation—e.g. alizarin blue. For special purposes chromic or ferric sulphate or chrome alum is employed. Alum or aluminium sulphate (8%), along with acid potassium tartrate (cream of tartar) (7%), is used for brighter colours—although the use of the usual mordanted wool in the mordanting process and ensure the penetration of the wool by the mordant, by preventing superficial precipitation through the action of ammoman liberated from the wool; it ensures the ultimate process of clearly, bright, dull 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. Copper can often mordant the same matter, but as a general 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, 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 (propylene oxide dissolved and passed into a cold solution of some metallic salt—e.g. aluminium acetate, basic chromium chloride, &c. The mordant is then fixed on the fibre as a metallic oleate, and after a passage through water containing a little chalk, is washed until the water is clear, and finally, a 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 done by steeping the cotton in a cold solution of tannic acid or in a cold decoction of some tannin matter, &c. 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 cellulose, but those mentioned are those most regularly employed. One of the 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., the case is the same, inasmuch as 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 dying treatment 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 carbonate to the dyebath; this becomes solid and separates in the vat when the 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 “stufing,” and the subsequent developing of the colour in and by application of dyestuff being termed “drawing.”

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 salt attracts and chemically combines with the colouring matter, producing the true or true dye, which is the dye which thus becomes dyed. The mode of applying the mordants varies according to the nature of the fibre and the metallic salt employed, the mordants being generally applied at present in the form of a basic or insoluble metallic compound, when boiled in their solutions. This colour is not fast to heating and a washing of the solution, but it is chiefly due to the action of the filler itself. The exact nature of the substance fixed on the fibre has not in all cases been determined, probably it is a compound of the metallic oxide and some organic base—e.g. a compound of the metallic oxide and amido base. The most mordanting wool depends upon its property of decomposing metallic salts, and fixing upon itself an insoluble metallic compound, when boiled in their solutions. This colour is not fast to heating and a washing of the solution, but it is chiefly due to the action of the filler itself.
for the production of pale shades which require to be very even and more permanent. There is still another method of achieving these
Colours in wood-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 categories of mordants 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
Natural Mordant Colours, the most important of these being included in
the following list.—Madder, Cochinile, Peachwood, Saphanphon, Limawood, Canwood, Barwood, Sanderswood, Old Fustic, Young Fustic, Quercitrin Bark, Persian Berries, Weld, Logwood.

so-called Flavin is a commercial preparation of Quercitrin
Bark, or the yellowing of quercitrin or of quercetin; it is much used
by woody-dyes for the preparation of bright yellow and orange
Colours. Wool is dyed in single bath by boiling with a mixture of Flavin
(8%), stannous chloride (4%) and oxalic acid (2%). Flavin
is used in very small quantity along with cochinile 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
of Persan Berries are similar to those of Quercitrin Bark, the orange colour given
with tin mordant being particularly brilliant. The use of this
dyestuff causes its employment to be somewhat limited. The colouring
matter of Persian Berries is called xanthorrhamin, which
extraction of fermentation and acid yields the true dyestuff
rhhamnitr.

Weld is the dried plant Reseda luteola, a species of wild mignonette,
formerly largely cultivated in Europe. Its dyeing properties resemble
those of Quercitrin Bark. The orange colour given
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
Lougwood 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
iron mordants, it produces a dark blue; and 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
boiling the wool is soaked in a solution of bichromate of
potash and the wool is then immersed in the dye solution. The wool is
allowed to stand covered for a short time, then it is boiled, and
finally tawed to expose it freely to the air. By
boiling the wool the colouring principle haematoxylin which lodgwood
contains is changed into the yellow colouring
matters. The constitution of this colouring matter has been recently discovered;
it is very closely allied to the brazili of peashwood, saphanphon
and is also a member of the γ-yron group of colouring
matters.

The importance of the above-mentioned natural dyestuffs is
ggradually diminishing in favour of mordant dyestuffs and other
artificial dyes of coal-tar. The natural dyestuffs are 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
anthraquinone (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 antrachene; they are
now largely employed, and Logwood is by far the most
Alizarin Colours is therefore inappropriate. The property, which Mordant
Colours possess in common, of combining with metals and produc
ting lakes, which readily adhere to the fibre, depends upon their
structure. The highly coloured species of haematoxylin, which owe their
relative position in the molecule of certain side atomic groups.
In alizarin there are, for example, two characteristic hydroxyl
groups of the compound occupying a special (ortho) position in the molecule,
that is they are next to one another. In the normal ketone
molecules, C-O. In other Mordant Colours there are
carboxyl (COOH) as well as hydroxyl groups, which are all
imported 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. NH₂, HSO₃ &c.,
which modify the colour as to solubility or hue. Hence it is that
the mordanting property of Alizarin Colours and related dyeing
matters, but rather as colouring principles, because they only
yield useful dyes in combination with metals. 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 silk and wool. Other Mordant Colours, e.g. many of the
Direct Colours and others, are capable of dyeing either vegetable
or animal fibres without the aid of a mordant; they are fully
deployed colouring matters in themselves, and possess the
mordanting property as well. The constitution of the various
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 a one colour with the different oxides, and are only
suitable for North American and animal fibres without mordants;
some are Direct Colours possessing mordant-dyeing

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

Galloferrin is used in wool and silk dyeing on chromium mordant as a base for fast shades, yielding yellow dyewoods, to furnish the yellow part of compound shades.

The alizarin yellows, R and GG, and gallicmone yellows, diamond flavine, chrome yellow, diamond yellow, carbasol yellow, chrome yellow and the others are Direct and Fast shades, respectively.

They also serve as substitutes for fuscous 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.

Koinferrin was employed in making 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 cotton with chromium mordant, an olive-green.

Coerulein S is the more soluble basic sulphate compound of the ordinary coerulein. It is applied in the same manner, 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 fuscous acid to light.

Fast Green, Dioxin and Gambine are chiefly used in calico-printing and in wool dyeing. With iron mordant they yield olive-green, which on wool produces a fast colour. Cotton is impregnated with ferrous acetate, dried, aged and washed with a mixture 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 may be dyed directly on 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 its being better on wool than on cotton, was 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 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 replaced them as substitutes for indigo. They are all 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 qualities of the fabrics, are very satisfactory, but it is necessary to mordant with acetic or sulphuric acid, and the dye is applied in the same manner as the alizarin blues.

Gallicmone Blue and Chrome Blue dye purplish blue and bright blue respectively, and are applied in the same manner as the mordanted alizarin blues.

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.

Alizarin Sulfate, Alizarin Viridine and Alizarin Saphiro 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 bright and very fast to light, and 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 saphiro dyes clear blue shades which are no less than much more brilliant 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 not very 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, the dyeing is repeated for a few minutes, and the dyeing is then finished by the addition of chromic acid.
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Bichromate of potash (2%) is added, and boiling is continued for half an hour longer.

The eriochrome colours (black, brown, red, &c.) are applied in wood dyeing like diamond black.

Chromate, of which there are several brands, is an Acid Colour which dissolves 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 is precipitated, and combined with the dyes.

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 separately. (Catechu, for instance, 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 reduced to 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, where-by it is converted into indigo-tin-disulphonic acid (Indigo Extract), which is readily soluble in water. This substance belongs to a 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 consists in reducing the influence of the indigo by means of alkalis (i.e. substances capable of yielding nascent hydrogen) indigo blue is changed into indigo white, which is soluble in alkali, the solution thus obtained finds its use in dyeing. To this end, the vat is 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 converted into indigo blue within and upon the fibre, which thus becomes dye. This is the true method and it is called the indigo method. Since this is a dyeing process, the water 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 mixture is 1 part aniline salt, 12 parts potash and 1 part indigo. The indigo is dispersed in the aniline solution and then introduced into the fibre. This mixture is more 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 mixture is 1 part aniline salt, 12 parts potash and 1 part indigo, the mixture is first 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 air. The material is then dried in 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 water being necessary to remove the salt.

In the method, employing the first-mentioned solution, chloride of copper is formed, and this being a very unstable compound, readily decomposes, and the aniline is oxidized by the copper. In the other solution, a 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 a base yields a dark brown amorphous substance. This further oxidation of emeraldine yields nigralline, 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 may be called a yellow oxidaniline. It is developed in ordinary aniline blacks during exposure to air. By a supplementary oxidation with chromic acid such a black is rendered ungreenable, the nigralline being probably changed into the more stable compound of naphthol.

Catechu is a valuable brown dyestuff, obtained from various species of Acacia, Arca 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 paste consistency. Catechu is largely employed 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 and 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 (1 oz. per gallon), then washed and dried.

Chrome Yellow is only useful in cotton-dyeing as a self-colour, or for conversion of an orange shade, with 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 slowly to a rich orange by a slight passage through boiling milk of lime, and at once washed with water, a basic compound of lead being thus produced. The colour is fast to light, but has the defect of being blackened by sulphuretted hydrogen.

**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 actual 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 attack 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 sulphuric acid. Cotton is dyed by first immersing it in a solution of manganese chloride, then dyeing and passing into a hot solution of caustic soda. There is thus precipitated on the fibres manganic hydrate, which by a short passage through a 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 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," "silver" 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 of 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 hydroextractor (centrifugal machine). The drying of the dyed and washed yarn is generally effected by suspending it 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 into the next, and the same thing occurs in the second (third and fourth in a four-box machine) box A, whence they are delivered through a second pair of squeezing rollers S 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 that it 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 copy-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 constitutes 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 copy-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
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 the pieces which are batched 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 \( B \) 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 used more for preparing (mordanting, &c.) than for dyeing.

For the dyeing of pieces in rope form a so-called “dyebecK” 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 endless 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, woolen and worsted yarn and piece goods of the worsted 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 slight 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 subject it to heat. 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 dry.

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 their 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 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 chromophore groups, e.g. \( \text{NO}_2 \), \( -\text{N}:-\), &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. \( \text{OH}, \text{NH}_2 \). These Witt terms auxochromes groups. In this way the chromogen \( \text{tri-nitro-benzene}, \text{C}_6\text{H}_4(\text{NO}_2)_3 \), becomes the dye stuff \( \text{tri-nitro-phenol} \) (picric acid), \( \text{C}_6\text{H}_4(\text{NO}_2)_2(\text{OH}) \), and the chromogen \( \text{azo-benzene}, \text{C}_6\text{H}_4\text{N}:-\text{N}:-\text{C}=\text{N} \), is changed into the dyestuff \( \text{azo-azo-benzene} \) (Fast Yellow), \( \text{C}_6\text{H}_4\text{N}:-\text{N}:-\text{C}=\text{N}(\text{NH})_2 \). 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 (NH) 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 (COOH) and the sulphononic acid (HSO\( ^{-} \)) groups; these either increase the solubility of
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 A. Cie. is white, while its unknown 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 chromophoric groups they contain, whereas the classification according to their mode of application is dependent upon the character and arrangement of the auxochrome 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 exhibit 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 decolourising 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 withholds 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 of the fibre. In the case of colours which are dyed on mordanted, 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 degrees of light and shade appear to the eye—blue, for example, appearing a darker grey, yellow, a lighter grey, in the printed photograph.

Since the year 1836, 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.

Conclusion.


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