

**DYEING** (OF. *dye*, to dye, AS. *dēagian*, from *dēag*, color; connected with AS. *dēaw*, dew). The art by which various substances, especially textile fibres, are impregnated with coloring matters with sufficient tenacity to resist the action of light, water, or ordinary wear.

**History.** The art of dyeing was practiced in some form by all primitive peoples. It is mentioned in the Bible that Jacob gave his favorite son Joseph a coat of many colors, and Moses tells how the skins of the ram and the badger used in the tabernacle were dyed red. The so-called Tyrian purple was known in the early days of the Roman Empire. It was such an expensive dye that the Emperor and the Imperial family were practically the only users of it, which gave rise to the expression "born to the purple." By an edict of the Emperor Diocletian, issued 301 A.D., the price of wool well dyed with this color was fixed at the equivalent of \$350 in gold per pound. According to Pliny, the purple color was derived from certain shellfish, a species of snail, found along the coast of Phoenicia. In time the shellfish became almost exterminated, and by the Middle Ages the dye had been lost to commerce. Recently a German color chemist, Dr. Friedländer, collected a sufficient number of the shellfish, which are still to be found along the shores of the Mediterranean, to extract the coloring matter and analyze it. It proved to be a combination of indigo and bromine. Neither the natural color nor its synthetic reproduction is of present-day importance. Pliny is also the authority for the statement that methods of dyeing black, yellow, and green were brought into Greece from India on the return of Alexander the Great. Some dyes probably of Indian origin are indigo, similar to the wood which Julius Cæsar found in use among the Britons; turmeric, or Indian saffron; cutch; and gambier. Towards the close of the Middle Ages the art of dyeing was greatly developed in northern Italy, especially in Florence, where the dyestuff archil (q.v.) was discovered about 1300. The early voyagers to America brought back with them new and valuable dyestuffs, such as cochineal, logwood, quercitron, and fustic. Subsequently dyeing developed according to the discoveries of new dyestuffs such as the mineral dyes, and the application of improved processes, until 1856, when the first artificial dyestuff, mauve, was discovered by William Henry Perkin in experimenting with aniline. Many aniline colors and other coal-tar dyes followed, until now dyes of this class have almost entirely superseded the natural dyestuffs. (See COAL-TAR COLORS.) The

NATURAL DYESTUFFS	ARTIFICIAL DYESTUFFS THAT HAVE DISPLACED THE NATURAL ONES FOR COTTON	ARTIFICIAL DYESTUFFS THAT HAVE DISPLACED THE NATURAL ONES FOR WOOL AND SILK
Quercitron (Still used along with logwood for printing).	<i>Diamine fast yellow</i> , B. A. (C.), <i>Chloramine yellow</i> (C.), <i>Chrysophenine</i> (C.), <i>Auramine</i> (H. G.), <i>Diamine yellow</i> (H.), <i>Chrysamine</i> (H.), <i>Thioflavine</i> (G.).	The different mordant-coloring yellows; also, <i>Naphthol yellow</i> , S. (H.), <i>Tartrazine</i> , <i>Quinoline yellow</i> (H.).
Persian Berries (Still much used in cotton printing and with tin salts, but little for wool).	For direct printing, <i>Auramine</i> , <i>Thioflavine</i> , T. (C.), the latter exclusively for discharges; also, <i>Chrysophenine</i> (H.), <i>Chloramine yellow</i> (H.), <i>Oriol</i> (G.). Important are also colors like <i>Alizarin yellow</i> (H.).	For silk: <i>Tartrazine</i> , <i>Fulling yellow</i> (C.), <i>Naphthol yellow</i> , S. (H.).
Weld		<i>Naphthol yellow</i> , S., <i>Fast yellow</i> (C.), <i>Tartrazine</i> , <i>Fulling yellow</i> (C.), <i>Citronine</i> (G.), <i>Jasmine</i> (G.), <i>Azoyellow</i> (H.), <i>Fast yellow</i> (H.), <i>Alizarin yellow</i> (H.).
Fustic (Still used for printing in connection with logwood and for dyeing wool).	Same as for Quercitron; also: <i>Sun yellow</i> (G.), <i>Diphenyl fast yellow</i> (G.), <i>Cresotin yellow</i> (G.); further, <i>Alizarin yellow</i> and its homologues (H.).	<i>Anthracene yellow</i> (C. G.), <i>Chrome yellow</i> (C. G.), <i>Mordant yellow</i> (C. G.), <i>Fulling yellow</i> (C.), <i>Azoyellow</i> (H.), <i>Fast yellow</i> (H.), <i>Alizarin yellow</i> (H.).
Logwood (Still used as extensively as before, for silk).	<i>Aniline black</i> , <i>Diaminogen black</i> (C.), <i>Diamine black</i> (C.), <i>Oxydiamine black</i> (C.), <i>Columbia black</i> (G.), <i>Direct deep black</i> (C.), <i>Vidal black</i> , <i>Immedial black</i> (G. H.), and similar sulphated products.	<i>Naphthol</i> and <i>Naphthylamine black</i> (C. G. H.), <i>Brilliant black</i> (C. G.), <i>Diamond black</i> (C. G. H.), <i>Wool black</i> (C.), <i>Alizarin black</i> (G. H.), <i>Anthracene black</i> (C. G.), <i>Azoacid black</i> (H.), <i>Chromotrope</i> , S. (H.).
Brazilwood	<i>Diamine fast red</i> , F. (C.), <i>Congorubin</i> (C.), <i>Diamine bordeaux</i> (C.), <i>Benzopurpurin</i> (G. H.), <i>Diamine red</i> (H.), <i>Fuchsin</i> (G. H.), <i>Hessian purple</i> (G.), <i>Saffranine</i> (H.), <i>Paranitraniline red</i> (H.), <i>Alizarin red</i> (H.).	<i>Cloth red</i> (C.), <i>Wool red</i> (C.), <i>Acid fuchsin</i> (G.), <i>Fast red</i> (H.), <i>Archil substitute</i> (G.), <i>Ponceau</i> (H.), <i>Apollo red</i> (G.), <i>Rocellin</i> (G.); in the fulling industry, <i>Alizarin red</i> (C. H.), <i>Diamine fast red</i> (C.), <i>Chromotrope</i> (H.).
Cochineal (Still used to some extent).		Vivid acid wool colors such as <i>Azoosin</i> (G.), <i>Chromazon red</i> (G.), <i>Palatine scarlet</i> (H. C.), <i>Brilliant crocein</i> (H.), <i>Brilliant cochineal</i> (C.), and the different <i>Ponceaux</i> , etc.
Archil (Almost entirely displaced).		<i>Acid fuchsin</i> (C.), <i>Azocarmine</i> (C. G. H.), <i>Archil substitute</i> (C. G. H.), <i>Azofuchsin</i> (C. G. H.), <i>Lana fuchsin</i> (C.), <i>Azorubin</i> (C.), <i>Azoacid fuchsin</i> (H.), <i>Rosindulin</i> (G.), <i>Apollo red</i> (G.), <i>Chromotrope</i> (H.).
Annatto	Orange colors, as <i>Chrysophenine</i> (H.), <i>Mikado yellow</i> and <i>orange</i> (H.).	
Safflower	<i>Rhodamine</i> (C. G.), <i>Erica</i> (C.), <i>Diamine rose</i> (C.), <i>Geranine</i> (C.), <i>Saffranine</i> (H.), etc.	
Berberin (Still used to some extent for dyeing silk).		Same as for WELD.
Catechu (Still much used, especially in combination with logwood, for silk).	Diamine colors, <i>Benzo</i> and <i>Congo</i> colors with supplementary treatment with chrome and copper, recently competed successfully (C.) and <i>Chrysoidin</i> (H.), <i>Vesuin</i> (H.), etc. <i>Alizarin</i> colors (partly in calico printing).	
Indigo	<i>Synthetic indigo</i> , <i>Indoin</i> (C. G. H.), <i>Naphthindon</i> (C.), <i>Fast cotton blue</i> (C.), <i>Methylene blue</i> (C. H.), <i>Indamine blue</i> (H.), <i>Janus blue</i> (H.) and the direct coloring and diazotizable blues of the Diamine, Diphenyl, and Benzo color groups. [Diamine blue and related colors (H.), <i>Diaminogen blue</i> , C. H.] A new product, <i>Immedial blue</i> (C. H.), belonging to the sulphated colors, seems to be among the most important substitutes. In calico printing natural indigo has been in part replaced by the <i>Synthetic Indigo</i> preparations and by the different basic blues, including <i>Nitroso blue</i> , <i>Alizarin blue</i> , etc. (C.).	<i>Alizarin blue</i> (C. G. H.), <i>Synthetic indigo</i> , <i>Alizarin cyanin</i> (C. G. H.), <i>Anthracene blue</i> (G. H.), <i>Chromotrope</i> , F. B. (H.), <i>Gallamite blue</i> (G.), <i>Gallocyanin</i> (G.), <i>Sulphocyanin</i> (C.), <i>Lanacyl blue</i> .

most important natural and artificial coloring matters may be found described in articles under their special names. Mineral and vegetable dyes were formerly considered more lasting than the artificial ones, but this view has in most cases positively no foundation in fact. The accompanying table shows which artificial substances have either partly or completely displaced natural ones in the dyeing of animal and vegetable fibres.

Dyestuffs may be divided into "basic colors," which dye vegetable fibres only after the use of an acid mordant, and "acid dyes," which require basic mordants for the same fibres. Both classes dye animal fibres direct without a mordant. A newer class known as "substantive dyes" can be used with both vegetable and animal fibres without mordanting. Most of the older aniline dyes belong to the first class; alizarine and sulphurated dyes to the second class; the newer azo dyes to the third class. (See *Azo Colors*, under the article COAL-TAR COLORS.) Based on their methods of application, most of the dyestuffs used at the present time fall into the following classes: acid, basic, substantive, mordant, after-chromed, developed, naphthol, coupled, sulphur, indigo or vat, oxidized, and mineral pigment dyes.

**Mordants.** These are substances capable of combining with other substances (the commercial dyestuffs) to form insoluble colored compounds. Thus, aluminum salts make an insoluble red compound with alizarin and are therefore used as mordants in calico printing. Ferric salts make, with alizarin, an insoluble dark purple compound and are likewise employed as mordants in calico printing. Soluble mordant salts must themselves be transformed into insoluble compounds before they are allowed to form the dyes in order to prevent the mordanting material from being dissolved out of the fabric when the latter is introduced into the dye bath. Therefore, after the fabric has become impregnated with the soluble mordant salt, it is treated with ammonia, lime, or hot steam—with a view to transforming the soluble salt into an insoluble hydroxide or an insoluble basic salt; or else the fabric is treated with sodium phosphate or sodium arsenate—with a view to transforming the soluble salt into an insoluble phosphate or arsenate. In the case of animal fibres the same end is often attained by simply immersing the fabric in a boiling dilute solution of the soluble salt, the insoluble mordant being then deposited in the fibre directly. The fabric containing the insoluble mordant is ready to be treated with the dyeing substance, the resulting color of the fabric being evidently that of the compound formed by the latter with the mordant. Another method of dyeing with the aid of mordants, extensively employed in calico printing, consists in mixing the dye directly with the soluble form of the mordant and with starch, dextrin, gum, or some other thickening substance, printing the mixture on the fabric, and then subjecting the latter to a process of steaming. The result is of course the same as in case the other methods are employed; for the steaming process has the effect of transforming the soluble into an insoluble form of the mordant, the latter then combining with the dyeing substance. Mordants may be either basic or acid—the former combining with "acid dyes," the latter with "basic dyes." The mordants mentioned above are

basic, and their compounds with dyes are termed "lakes." Among the acid mordants may be mentioned tannin, or tannic acid. After the fibre has been impregnated with this mordant in its ordinary, soluble form, it is passed through a weak solution of chloride of tin or of tartar emetic. These produce respectively the tannate of tin or the tannate of antimony (tartar emetic is a compound of antimony), and these insoluble tannates further combine into insoluble colored compounds with dyes.

**Theories of Dyeing.** The question as to whether dyeing involves true chemical combination of the fibres with the dyestuffs or not has not yet been definitely answered. Some investigators believe that dyed fibres are merely mechanical mixtures; others hold that dyed fibres are true chemical compounds; finally, still others hold that they constitute what are now termed "physical mixtures," or "solid solutions." Those who accept the chemical theory argue that if the dyestuff did not combine chemically with the fibre, then there would be no reason why chemically neutral-colored substances should not act as dyes; yet true dyes are generally either acid or basic, while the fibres themselves may be either basic or acid, or else may include both basic and acid constituents. Another argument in support of the chemical theory is found in the fact that some substances, while themselves colorless, are capable of imparting color to fabrics when directly applied to them; the view being that colored substances must be transformed chemically in order to produce color. The principal arguments in favor of the "physical mixture" theory, advanced by O. N. Witt in 1890, are as follows: 1. Solid fuchsin is green, with a metallic lustre; solutions of fuchsin are colored red; and fabrics dyed with fuchsin are likewise colored red. 2. Solid rhodamine shows no trace of fluorescence; its solutions are fluorescent; and silk dyed with rhodamine likewise shows distinct fluorescence. The fact that the same dyestuff may impart different colors to different fabrics is compared with the fact that iodine gives different colors in different solvents, and yet there is no reason for assuming that iodine forms chemical compounds with its ordinary solvents. Finally, in accordance with Witt's theory, the function of mordants is explained by the assumption that solutions of these substances in fibres are much better solvents for the dyestuffs than are the pure fibres. However, while interesting because capable of development and quantitative verification, this physicochemical theory is yet far from being definitely established or generally accepted by chemists.

**Dyeing Processes.** Cotton, silk, artificial silk, and wool are the textile fibres that are usually subjected to processes of dyeing. Before dyeing, the fibres are first cleaned so as completely to remove all natural and artificial impurities, such as grease and dirt, which tend to produce spots or uneven shades of color, in consequence of improper fixing of the mordant and color. Whenever light and delicate tints are to be dyed on the fibre, bleaching becomes necessary. The preliminary steps in the preparation of cotton include boiling the fibre in a weak solution of caustic lye, after which it is rinsed and then steeped in a solution of bleaching powder and again rinsed. A further step consists in steeping it in dilute sulphuric, hydro-

chloric, or acetic acid, after which it is again cleansed by washing, and dried. Silk is boiled in soap solution in order to remove the natural silk glue which accompanies the crude fibre and is then bleached either by exposure to sulphurous acid fumes produced by burning sulphur or by the use of the peroxides of hydrogen and sodium. Wool is cleansed by washing in warm soap solution, frequently combined with sodium or ammonium carbonate, by means of which the natural grease of the fibre is removed. It is then bleached with sulphur dioxide.

**Apparatus.** The apparatus of the dyer is very simple, consisting of vats, kettles, and cisterns, which may be of wood, stone, or metal. In Europe the kettles are still heated over open fires, but in America a steam coil is universally used. A pure water supply is absolutely essential to successful dyeing. When the available water supply is contaminated by sewage or the water is hard because of lime salts, artificial purification must be employed. Suspended matter may sometimes be removed by sedimentation or filtration, or the two combined, but chemical treatment may be required to remove these and other impurities.

Dyeing may be done in various stages of fabric manufacture, depending upon the material and the purpose for which it is intended. Some of the methods employed are:

1. *Raw-Stock Dyeing.*—This is also known as dyeing in the wool. The wool is dyed after scouring, and after bleaching if the latter is necessary, but before it is carded or spun. The dye penetrates the fibre well, giving a permanency of color desirable in garments destined for hard wear. In the Oxford mixture the black is generally dyed in the wool.

2. *Dyeing in the Slub.*—The slub, or top, is the soft rope of fibres formed in the processes preparatory to twisting and spinning. Dye-stuffs penetrate it readily. A special machine is in use which prints the dye upon the slub at regular or irregular intervals. Later drawing and twisting give a well-mixed effect to the yarn. Such yarns are used for the Vigoureux mixture.

3. *Skein Dyeing.*—The yarn is dyed in the skein. Ginghams and woollen plaids are skein dyed.

4. *Piece Dyeing.*—The material is dyed after weaving.

5. *Cross Dyeing.*—This method is applied to wool and cotton mixtures. Dyes are used for wool which are fugitive on cotton; therefore the wool takes the dye, and the cotton remains unchanged. White hair-line or check effects are produced in this way. If a single color is desired, the cotton is dyed first to the right shade, then the material brought up to uniform color in a wool bath.

6. *Resist Dyeing.*—This is a form of cross dyeing. Certain yarns, or parts of fabrics, are treated to resist the dye which colors the remainder of the material. The Javanese employ this method in their Batik work.

7. *Discharge Dyeing.*—By the use of chemicals the color is discharged from dyed material, in polka dot or other pattern effects.

In all dyeing operations considerable attention must be paid to the permanency of the dye used. Dyes may be fast to light, to washing, or to both. The choice of dyestuff as to fastness is determined by the purposed use of

the material to be dyed. A color is considered fast to light if it does not fade with four weeks' exposure to the sun; moderately fast if only a slight fading is observed after three weeks, and fugitive if it fades in one week.

**Bibliography.** The literature of dyeing is very extensive, and reference should be had to the articles in the various technical cyclopædias as well as to the following works: Crookes, *A Practical Handbook of Dyeing and Calico-Printing* (London, 1874); Hurst, *Silk Dyeing, Printing, and Finishing* (Glasgow, 1892); Knecht, Rawson, and Lowenthal, *A Manual of Dyeing, for the Use of Practical Dyers, Manufacturers, Students, and All Interested in the Art of Dyeing* (London, 1893); Fraps, *Principles of Dyeing* (New York, 1903); Dyer and Color-Maker's Companion (Philadelphia, 1898); *Recent Progress in the Industries of Dyeing and Calico-Printing*, being a supplement to Sansone, *The Printing of Cotton Fabrics* (Manchester, 1895); id., *Dyeing* (ib., 1897); Sattler, *Industrial Organic Chemistry* (Philadelphia, 1900); Cain and Thorpe, *The Synthetic Dye Stuffs* (London, 1905); Pellew, *Dyes and Dyeing* (New York, 1913); Matthews, *Laboratory Manual of Dyeing and Textile Chemistry* (ib., 1913); and Yearbooks issued by the various color houses. See TEXTILE PRINTING; COAL-TAR COLORS; MINERAL COLORS; MORDANTS; and special articles on dyestuffs.