

obtained a violet dyestuff by oxidizing impure aniline with chromic acid, took out a patent for it, and commenced manufacturing it in England. Many other dyes were subsequently obtained from aniline and the substances related to it, by A. W. Hofmann, Gries, Girard, Lauth, and many others. But the most sensational step was the preparation by Graebe and Liebermann (1868) of a natural dyestuff, viz., the coloring principle of madder root, from the anthracene of coal tar. In 1880 indigo was first prepared, not from coal-tar products, but by a purely synthetic method, and other natural colors have since been prepared in a similar manner; so that natural dyestuffs reproduced by artificial means need not necessarily originate from coal tar. The artificial indigo and alizarin are not mere substitutes for the natural indigo and madder; they are chemically identical with them and surpass them in purity, and their adaptability to special methods in dyeing and printing makes them even more desirable. The color industry was first developed in England and France, but the more thorough technical instruction at the German universities produced a body of skilled manufacturers and investigators who soon took the lead. At present, in addition to the great factories near Berlin, Frankfurt, Elberfeld, and Mannheim, and a host of smaller ones in various parts of Germany, German capital controls many of the establishments in France, Russia, and other countries. The United States possesses few independent factories, and the list of their products is rather limited; indeed, American dyers appear to call for a smaller range of dyestuffs than those of other countries. A peculiar modern development has been the extension of the methods of the dye industry to the production of artificial drugs, such as antipyrin, antifebrin, etc., many of which are manufactured in the same establishments which control the dye patents.

**Classification.** Artificial colors were formerly classified merely according to the sources from which they were obtained. Thus, many of them, including magenta, "aniline blue," "aniline green," "aniline yellow," etc., were grouped together as *aniline colors*. At present somewhat different systems of classification are used by different authors, but all systems are based exclusively on the chemical constitution of the dyes.

Many attempts have been made to find a general answer to the question, What must be the chemical nature of a carbon compound in order that it may be a dye? An all-embracing answer to this question has not yet been found. But experience has shown that the true dyestuffs exhibit peculiar groupings of the constituent atoms. Such "chromophore" groupings produce, however, only a *tendency* towards color, but not necessarily colors; indeed, many compounds containing them are perfectly colorless, and the majority of true dyes become colorless if deprived of the small amount of oxygen they contain, although their chromophore groups may not be in the least affected. If, however, a chromophore group is combined with certain other atomic groups known as auxochromes, the result is a dye. For example, the so-called *azo group* ( $-N=N-$ ) is chromophoric; the compound called azobenzene,  $C_6H_5-N=N-C_6H_5$ , although colored red and evidently containing the azo group, is not a dye; but it becomes one when the so-called amido group ( $NH_2$ ) also is

**COAL-TAR COLORS.** Coloring matters artificially prepared from coal tar, chiefly from the hydrocarbons extracted from it. (See COAL TAR.) The first observation of a colored compound of this class was made by Runge in 1834; but the real beginning of the great modern color industry dates from 1856, when W. H. Perkin

introduced into its molecule, the compound  $C_6H_5-N=N-C_6H_4NH_2$ , called amidoazobenzene, being a true dye. If, instead of the amido group, a hydroxyl group (OH) is introduced, the result is again a dye (an orange one). Further, the tints of dyes are produced by variation in the "substituting" groups which replace hydrogen in the primitive molecule. Thus, the introduction of the methyl group ( $CH_3$ ) generally increases the violet tendency; the phenyl group ( $C_6H_5$ ) produces bluish tints; the naphthyl group ( $C_{10}H_7$ ) a tendency towards brown-red; etc. The relative position of the groups likewise plays a large part in the determination of color. But, as we have already observed, a definite and all-embracing rule does not exist. Frequently compounds must enter into combination with a base or an acid before they will fix themselves upon the fibre, and then the tints are frequently affected by the different bases or acids to a varying degree. For example, alizarin dyes red with the hydroxide of aluminum, and black with the hydroxide of iron.

For the purpose of the present sketch the coal-tar colors may be grouped in five classes: viz., the azo colors; triphenylcarbinol derivatives; quinone derivatives; diphenylamine derivatives; and indigo dyes.

**Azo Colors.** The characteristic compound of this class is azobenzene,  $C_6H_5N=NC_6H_5$ , already mentioned above. We have seen that the introduction of either  $NH_2$  or OH in place of a hydrogen atom produces a coloring matter—yellow in the former, orange in the latter instance. Replacing either or both of the phenyl groups ( $C_6H_5$ ) by more complex hydrocarbon groups deepens the tone (with a tendency towards the redder tints), increases the affinity for fibres, and diminishes the liability to fade. The earlier dyes of this class, such as "aniline yellow," "Bismarck brown," chrysoidin, etc., were singularly brilliant, but were not fast; whereas the browns and the many reds, ranging from scarlet to purple, which are now produced under the names of ponceaux or bordeaux, congos, quinoline red, etc., are exceedingly permanent. In manufacturing this class of dyes nitrous acid is allowed to act upon an ice-cold solution of the salt of any primary base (like aniline), and the "diaz salt" formed is allowed to act on another base or a phenol; an endless variety of combinations is thus possible.

**Triphenylcarbinol Derivatives.** These represent the first discoveries in the aniline dyes, and some of them are still produced on the largest possible scale. The fundamental compound of the class is triphenylcarbinol ( $C_6H_5$ )<sub>3</sub>COH, and its derivatives are properly subdivided into *rosanilines*, *rosolic acids*, and *phthaleins*.

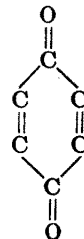
In the rosaniline group two or three amido groups ( $NH_2$ ) are introduced in place of hydrogen atoms of the phenyls ( $C_6H_5$ ). The *diamido* compounds are green; the *triamido* compounds are red, violet, or blue. Strictly speaking, the compounds thus obtained are not themselves dyes, but are bases which must first be combined with suitable acids and thus brought into a soluble form. Their salts are beautifully crystalline bodies in the solid condition, showing colors quite different from those of the solutions and having peculiar lustres like those of beetles' wings. The solutions have very intense colorations and stain animal fibres readily and permanently, although they do not fix themselves easily upon cotton or linen. They are the most

brilliant and lively dyes, but are strongly affected by sunlight and are consequently less useful than some dyes of other classes. They are generally manufactured by oxidizing processes at a comparatively high temperature, whereby two or three simpler compounds are welded, as it were, into compounds of complex molecular structure. Thus, in the manufacture of the well-known magenta dye (a triamido compound) approximately equal quantities of aniline, orthotoluidine, and paratoluidine are heated from 8 to 10 hours with arsenic oxide to 190° C. in large iron kettles. A very thick mass results, which can be extracted with hot water, and the compound thus obtained is found to be made up of molecular quantities of aniline, orthotoluidine, and paratoluidine, chemically combined.

Rosolic acid and its derivatives are made by the condensation of various phenols, three phenols being condensed into one compound of the rosolic acid group, just as three bases are condensed into one compound of the rosaniline group. The comparatively few dyes of this group give various shades of red. The hydroxyl groups, and hence the acid character of the phenols, remain unchanged in the products of condensation; the latter therefore combine with bases and then they readily go into solution.

The phthaleins differ from the rosolic acids in so far as one of the three phenyls of the triphenylcarbinol is connected in them with a carboxyl group (COOH), the other two phenyls having one or more hydroxyls apiece, as in the rosolic acids. The phthaleins were discovered by Adolph Baeyer and are chiefly remarkable for the fluorescence of their alkali salts in solution. They are prepared by heating phenols with phthalic anhydride and a little sulphuric acid; when resorcin is taken as the phenol a very well-known compound is obtained, which has been called *fluorescein*, while its sodium salt is known as *uranin*. Solutions of the latter are yellow, with a green fluorescence. This fluorescence is so intense that it is distinctly noticeable in extremely dilute solutions; so that this salt has been used to trace subterranean water-courses supposed to connect two neighboring bodies of water, the dye being thrown into one of these and fluorescence being subsequently noticed in the other. The potassium salt of a brominated fluorescein is *eosin*,  $C_{20}H_6O_6Br_2K_2$ , with a magnificent red and yellow fluorescence. The phenomenon of fluorescence is due to the action of light falling upon the solution. Some of the light rays, being reflected from the surface, carry one color to the eye; some are absorbed; some are emitted in the form of light waves with either a longer or shorter period than those which are absorbed, and thus produce a different color. Fluorescein and eosin emit shortened light waves.

**The Quinone Derivatives.** These contain the characteristic nucleus—



and are almost invariably colored, although they become suitable for dyes only when they also contain several hydroxyl groups. By far the most important substance of this class is alizarin (q.v.), which was already mentioned as identical with the active principle of madder. Anthracene (q.v.), a coal-tar hydrocarbon, is converted into anthraquinone by heating with potassium bichromate and sulphuric acid; the anthraquinone is acted upon by fuming sulphuric acid, and the resulting compound is melted with caustic soda, yielding a sodium salt of alizarin. This is soluble in water with a fine red color, but does not fasten upon any kind of fibre. If, however, cotton is previously impregnated with salts of aluminum, iron, or chromium, the alizarin will form insoluble salts ("lakes") with these metals; and as the precipitation occurs within the pores of the fibre, subsequent washing cannot remove it. Colors of this class of dyes are not suitable for silk and wool, but are very intense and permanent when properly applied to cotton.

**The Diphenylamine Derivatives.** These include many varieties of dyes, such as the indulins, indophenols, thiazins, etc. Their chemistry is too involved to be disposed of in a few words. It may, however, be mentioned that their characteristic groups are similar to anthraquinone, excepting that the oxygen of the latter is replaced by sulphur, imido groups, etc. The more important dyes of this class include "methylene blue" and "aniline black."

**Indigo Dyes.** By far the most important of these is indigo itself, a vegetable dye obtained from a tropical plant cultivated in India since the earliest times. The sap of this plant, when fermented under conditions excluding oxygen, yields *indigo white*, a soluble material having the formula  $C_{16}H_{12}N_2O_2$ ; if the fermentation proceeds in the open air, *indigo blue*,  $C_{16}H_{10}N_2O_2$ , is produced. This substance is a derivative of the base called indol,  $C_8H_7N$ , which occurs ready formed, in small quantities, in many animal and vegetable secretions. It can be prepared artificially from aniline and chloraldehyde. When indigo was found to consist of two indol molecules joined together and oxidized, the clue for the production of artificial indigo was at hand. It has since been found that any benzene derivative having a nitrogenous group and a two-carbon group in the "ortho" position may give rise to the formation of indigo. The first practical method, devised by Baeyer in 1880, involved the action of potassium hydroxide on orthonitropropionic acid; but many other methods have been devised since then, such as the action of melted potassium hydroxide on bromacetanilid, the action of halogenated acetone on aniline, etc. Indigo is one of the most reliable dyestuffs, both as to brilliancy and permanency in either its natural or its artificial form. The latter, however, gives a brighter shade than the average vegetable dye, being of uniform composition and free from the impurities of the natural indigo. Until recently, the finished compound could, however, only be applied after reduction to the soluble indigo white, and this made its use in dyeing and printing somewhat cumbersome. It was necessary to set up a fermentation vat in which the reducing action was allowed to continue for several days before the solution was in a form suitable for dyeing. At present rapid reduction is brought about by the use of sodium hydrosulphite in an alkaline bath,

or the indigo may be purchased already reduced and ready for immediate dyeing in an alkaline solution. Indigo is still called a vat color, and many new dyes of great permanency have been placed on the market recently, which, like indigo, are applied in the modern alkaline hydrosulphite vat and are grouped in this class. See INDIGO.

**List of Colors.** The following are some of the best-known commercial coal-tar colors, their molecular formulas, and the principal methods employed in their manufacture.

*Aldehyde Green.* See Aniline Green below.

*Alizarin*,  $C_{14}H_8O_4$ , made artificially by successive treatments of anthracene with chromic acid and fuming sulphuric acid, and melting the product with potassium hydroxide. Among the dyes allied to alizarin are: *Alizarin Black*,  $C_{16}H_8O_4.NaHSO_3$ ; *Alizarin Blue*,  $C_{17}H_9NO_4$ ; *Alizarin Orange*,  $C_{14}H_7NO_6$ ; and *Alizarin Violet*, or Gallein,  $C_{20}H_{10}O_7$ .

*Aniline Black*,  $C_{20}H_{22}N_8$ , made by the oxidation of aniline with mineral salts.

*Aniline Blue* (triphenylrosaniline hydrochloride),  $C_{25}H_{35}N_3Cl$ , made by heating rosaniline, benzoic acid, and aniline, and subsequently adding hydrochloric acid.

*Aniline Brown*, Bismarck Brown, or Phenylene Brown (triamidoazobenzene),  $C_{12}H_{13}N_5$ , made by the action of nitrous acid on metaphenylenediamine.

*Aniline Green*, or Aldehyde Green,  $C_{22}H_{27}N_3S_2O$ , made by the action of ordinary aldehyde on an acid solution of rosaniline sulphate and the subsequent addition of sodium hyposulphite.

*Aniline Orange.* This name is applied to various compounds made by the action of amidosulphonic acids on phenols. The name is often applied to the so-called Victoria Orange,  $C_7H_6N_2O_2$ .

*Aniline Red.* See Fuchsin below.

*Aniline Scarlet*,  $C_{18}H_{15}N_2O_4SNa$ , made by the action of diazoxylene on naphthosulphonic acid.

*Aniline Violet.* See Mauvein below.

*Aniline Yellow* (hydrochloride),  $C_{12}H_{12}N_3Cl$ , made by the action of nitrous acid on an excess of aniline.

*Auramin* (hydrochloride),  $C_7H_{24}N_3OCl$ , made by the successive action of phosgene gas (carbon oxychloride) and ammonia upon dimethylaniline.

*Aurantia* (ammonium salt of hexanitrodiphenylamine),  $C_{12}H_8N_6O_{12}.NH_4$ , made by the action of nitric acid on methyldiphenylamine.

*Aurin*,  $C_{19}H_{14}O_8$ , made by the action of oxalic and sulphuric acids on phenol.

*Benzaldehyde Green.* See Malachite Green below.

*Benzidine Red.* See Congo Red below.

*Benzopurpurins*, dyes of various scarlet shades. They are chemically allied to Congo Red (which see below) and are made by treating salts of toluidine (which is made from nitrotoluene, and is analogous to benzidine) with nitrous acid, and combining the resulting salts with  $\alpha$ - and  $\beta$ -naphthylamine sulphonic acids.

*Bismarck Brown.* See Aniline Brown above.

*Blackley Blue.* See Indulin below.

*Bordeaux.* See Ponceaux below.

*Chrysoidin* (hydrochloride),  $C_{12}H_{13}N_3Cl$ , made by the action of diazobenzene chloride on metaphenylenediamine in aqueous solution.

*Congo Red*, or Benzidine Red,  $C_{22}H_{22}N_6S_2O_4Na_2$ , made by the action of nitrous acid and then of sodium naphthionate on benzidine hydrochloride.

*Eosin*,  $C_{20}H_5O_3BrK_2$ , or  $C_{20}H_5O_3Br_2Na_2$ , made by the action of bromine on fluorescein.

*Erythrosin*,  $C_{20}H_5O_3I_2Na_2$ , made by the action of iodine on fluorescein.

*Fluorescein*,  $C_{20}H_{12}O_6$ , made by the action of phthalic acid anhydride on resorcin.

*Fuchsin*, Rosaniline Hydrochloride, Magenta, or Aniline Red,  $C_{20}H_{20}N_3Cl$ , made by the oxidation of toluidine and aniline in the presence of acids.

*Gallein*. See Alizarin above.

*Helianthin*. See Methyl Orange below.

*Indigo*. See text of the article above.

*Indulin*, or Blackley Blue,  $C_{18}H_{18}N_3$ , made by heating aniline salts with amidoazobenzene.

*Magenta*. See Fuchsin above.

*Malachite Green*, Benzaldehyde Green, or Victoria Green,  $3C_{23}H_{22}N_2Cl \cdot 2ZnCl_2 + H_2O$ , made by the condensation of benzaldehyde with dimethylaniline, and the subsequent addition of hydrochloric acid and zinc chloride.

*Martius' Yellow*,  $C_{16}H_8N_2O_3SNa$ , made by the action of nitric acid on  $\alpha$ -naphthol-monosulphonic acid.

*Mauvein* (hydrochloride), or Aniline Violet,  $C_{27}H_{22}N_4Cl$ , made by the action of chromic acid on aniline containing some toluidine.

*Methyl Orange*,  $C_{12}H_{12}N_3SO_3Na$ , made by the successive action of nitrous acid and methylaniline upon paraamidobenzene-sulphonic acid; it is the sodium salt of helianthin.

*Methyl Violet*,  $C_{24}H_{28}N_4Cl$ , made by oxidizing dimethylaniline with metallic salts.

*Methylene Blue*,  $C_{16}H_{18}N_3S$ , made by heating amidodimethylaniline with sulphide of iron.

*Naphthol Yellow*,  $C_{10}H_6N_2O_3SK$ , made by the action of nitric acid on  $\alpha$ -naphthol-trisulphonic acid.

*Night Blue*,  $C_{20}H_{16}N_3O$  (the hydrochloride of this is the commercial dye), made by heating pararosaniline with aniline and benzoic acid.

*Nigrosin*,  $C_{18}H_{16}N_3$ , made by heating aniline salts with nitrobenzene.

*Pararosaniline* (chloride),  $C_{19}H_{19}N_3Cl$ , made by oxidizing a mixture of paratoluidine and aniline with arsenic acid, or nitrobenzene.

*Phenylene Brown*. See Aniline Brown above.

*Ponceaux*, or Bordeaux. Various derivatives of azonaphthalene. "Ponceau 3R,"  $C_{19}H_{16}N_2O_7S_2Na_2$ , is made by combining diazocumene chloride with  $\beta$ -naphthol-disulphonic acid.

*Primulin*,  $C_{14}H_{12}N_2S(?)$ , made by the action of sulphuric acid on thiotoluidine.

*Resorcin Yellow*, or Tropæolin, O,  $C_{12}H_{10}N_2O_2S$ , made by the action of diazobenzene-sulphonic acid on resorcin.

*Rhodamine* (hydrochloride),  $C_{28}H_{31}N_7O_3Cl$ , made by the action of phosphorous trichloride on fluorescein, and treatment of the product with diethylamine.

*Roccellin*,  $C_{20}H_{13}N_2O_4SNa$ , made by the action of  $\beta$ -naphthol on the diazo compound of naphthionic acid.

*Rosaniline*. See Fuchsin above.

*Rose Bengale*,  $C_{20}H_4Cl_2I_2O_3K_2$ , made by the successive action of chlorine and iodine upon fluorescein.

*Rosolic Acid*,  $C_{20}H_{16}O_6$ , closely allied to aurin; neither aurin nor rosolic acid is specially valuable.

*Safranin*,  $C_{27}H_{21}N_4Cl$ , made by the oxidation of a mixture of toluylene-diamine and aniline or toluidine.

*Tropæolin*. This name is applied to various compounds made by the successive action of

nitrous acid and phenols upon amidobenzene sulphonic acids. See Resorcin Yellow above.

*Uranin*,  $C_{20}H_{10}O_3Na_2$ , the sodium salt of fluorescein (which see above).

*Victoria Green*. See Malachite Green above.

*Victoria Orange*. See Aniline Orange above.

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