

CHAPTER 5

DYES USE IN TEXTILE INDUSTRY

5-1 Cause of Color

A certain amount of unsaturation in the dye molecule, with part of it at least in the form of aromatic rings, combined the quinoid structure of a minimum complexity, usually lays the foundation for dyes. Much has been correlated between chemical structure and color, and the earlier conceptions promulgated by the dye chemists in this field are still helpful. We may write the equation.

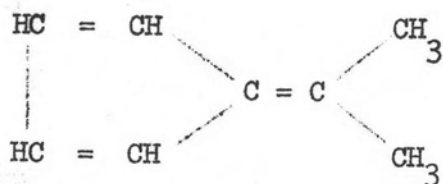


The chromogen is an aromatic body containing a group called a chromophore. By derivation, **Chromophore** means color giver, and is represented by such chemical radical as the following:

1. The nitroso group : $-\text{NO}$ (or = N-OH)
2. The nitro group : $-\text{NO}_2$ (or = NO.OH)
3. The azo group : $-\text{N} = \text{N}-$
4. The ethylene group : $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array}$
5. The carbonyl group : $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{O} \\ \diagdown \quad \diagup \end{array}$
6. The carbon-nitrogen groups : $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} - \text{NH} \text{ and } \text{CH} = \text{N}- \\ \diagdown \quad \diagup \end{array}$
7. The sulfur groups : $\begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{S} \text{ and } -\text{C}-\text{S}-\text{S}-\text{C}- \\ \diagdown \quad \diagup \end{array}$

Such groups add color to the simpler aromatic bodies by causing displacement of, or an appearance of, absorbent bands in the visible spectrum. These chromophores are so important that we chemically many of our dyes by the chief chromophore that they

contain. These chromophore groups are capable of reduction and if this is carried out, the color frequently disappears, probably because of the removal of electron resonance. Close packing of unsaturation, as conjugation, also tends toward color. Thus, even the hydrocarbon dimethylfulvene, has an orange color. Although it may be colored,



a chromogen may lack the chemical affinities necessary to make the color adhere to/ ^{the} textile fiber. Thus assistant groups, or auxochromes, are needed, which are usually salt-forming groups such as $-\text{NH}_2$, OH , their derivatives, or the solubilizing radicals $-\text{COOH}$ or $-\text{SO}_3\text{H}$. These auxochromes, chromophores, and chromogens will be very apparent by following the classification of dyes, but the assisting radicals such as $-\text{OH}$, $-\text{NH}_2$, $-\text{SO}_3\text{H}$, and $-\text{COOH}$ have usually more influence in the placing of a dye in a given use group directed toward dyeing a certain fiber, rather than in a chemical structural classification. (Shreve, 1967).

5-2 Testing of Dyes

In the use of dyes it is of the utmost importance to know such properties as fastness, solubility, and method of dyeing. There are various types of fastness for dyes, all relative to one another. American-made dyes are as fast as any others in the world, being the same chemical compounds here as abroad. (Shreve, 1967).

5-3 Classification of Dyes

Dyes are classified from both the chemical and the application, or end-use, viewpoints. The manufacturers look at dyes from the chemical aspect, and arrange and manufacture them in groups, usually of like chemical conversions; this frequently brings similar chromophores together. Thus dyes that contain the azo chromophore are found manufactured in a building that may be called the azo building. On the other hand, similarity in grouping of those that contain the indigoid radical is found. This very largely parallels the modern chemical-conversion way of classifying and looking at applied organic reactions. Not only do the factories arrange dyes in this way, but the books presenting the properties of dyes so classify them. (Shreve, 1967).

In this chapter the various dyes are discussed under this chemical classification. On the other hand, the users of dyes group them according to the methods of application. A dyer engaged in coloring silk is particularly interested in the type of dye that gives good results on this fiber, and not specially in dyes that color cotton only. There is not always this sharp differentiation in application; indeed, certain dyes are union dyes and will color more than one fiber. Three broad divisions of fibers are dyed: those products of vegetable origin, those from animals, and those made synthetically. Cotton, linen, and paper are of a vegetable nature and essentially consist of cellulose. On the other hand,

the products of animal origin are much more reactive and consist of such substances as silk, wool, feathers, fur, and leather. The man-made fibers consist principally of Nylon, Dacron, Orlon, Dynel, Acrilan, and of viscose rayon, the latter dyeing quite similarly to cotton, it being also essentially cellulose, and acetate rayon, which is an ester and requires disperse dyes. (Shreve, 1967).

Disperse dyes are those which have been specially developed to dye cellulose acetate and some of the new synthetic fibers. They may be broadly divided into two general groups, embracing insoluble simple azo dyes and insoluble aminoanthraquinone colors, both in a highly dispersed type, and consequently capable of penetrating, or dyeing, the fiber. Both of these general groups of dyes usually contain the ethanalamine $\text{-NHCH}_2\text{CH}_2\text{OH}$, or a similar radical which renders these dyes more readily dispersible in water and more easily absorbed. Early examples of the dispersed dyes are the SRA, wherein the dispersing agent is sulforicinoic acid (hence the designation SRA). Another example is CI 61100, Disperse Violet 1. (Shreve, 1967).

Acid dyes are used to color synthetic and natural (animal) polyamide fibers from acidified solution. Such anionic dyes are attached to the positively charged amine group in the fiber. The acid auxochrome or solubilizing groups, -NO_2 , $\text{-SO}_3\text{H}$, and -COOH , frequently aided by -OH , are usually present in the acid dye, whether the fundamental chemical structure is that of the azo, triarylmethane, or anthraquinone complex. These acid dyes are of importance in wool and silk dyeing. Such dyes are somewhat deficient

in fastness to alkalies and soap, though usually possessed of good light resistance. Examples are Orange II, CI 15510, Acid Orange 7, and Acid Black 10B, CI 20470, Acid Black 1 (the azos), and Acid Alizarine Blue B, CI 63010, Acid Blue 45. (Shreve, 1967).

Azoic dyes are direct and developed dyes, applied especially on cotton. These azoic dyes are essentially colorless azo dye intermediates, marketed in four different groups of products:

1. Simple arylamines or their mineral acid salts (color bases). These need ice, sodium nitrite, and mineral acid for diazotization before coupling.

2. Stabilized diazonium compounds (fast salts), which are made by combining diazotized arylamines with a precipitant, such as zinc chloride. These are stable products which are soluble in water and can be coupled on the fiber with a selected component. Either the color base after diazotization or the already diazotized fast salt can be reacted by the user in situ with the same coupling constituent to produce the same dye.

3. The Naphthol-group (Du Pont's Naphthanil) dye, by first impregnating the fiber with a selected coupling component, to which the diazotized arylamine is coupled in situ.

4. A group comprising mixtures of one selected triazene (made by combining a diazotized arylamine with a special type of secondary amine) and one selected Naphthol, resulting in a stabilized specific insoluble azo dye produced in situ by special printing and acid-aging techniques. These are marketed as Rapidogens (Du Pont Diagen brand) and are exclusively used for printing. The azoics

are next in importance to the vat dyes, which they surpass in brilliance of shade, particularly in the bright reds. (Shreve, 1967).

Basic dyes are mostly amino, or substituted amino, derivatives, frequently from the triarylmethane or xanthene class, but they are applied mostly to paper. Practically all the Auramine, CI 41000, Basic Yellow 2, manufactured in America is consumed in paper dyeing. Some basic dyes, Bismarck Brown, CI 21010, Basic Brown 4, and Chrysoidine, CI 11270, Basic Orange 2, are used for leather. Crystal Violet, CI 42555, Basic Violet 3, and Methyl Violet, CI 42535, Basic Violet 1, and 42535 B, Solvent Violet 8, are mainly employed in typewriter ribbons, carbon papers, and duplicating inks, where also some other basic dyes find application. A significant use of solvent basic dyes is in writing and printing inks. In the sulfonated form some special types of basic dyes still find a limited application in the dyeing of silk and wool, but a more important utility of these sulfonated forms is their conversion to lakes for printing inks. (Shreve, 1967).

Direct dyes are frequently from the azo class, and are used to dye cotton or the vegetable fibers. Some of them are also employed for dyeing union goods (cotton and wool or cotton and silk). As this dyeing is usually aided by the addition of common salt, or Glauber's salt, to the dye bath, such dyes have been called salt dyes. The salt decreases the solubility of the dye, and hence causes better exhaustion of it from the dyeing solution. Like acid dyes,

they are anionic: however, their differences lie in the structure of the dye molecule. To be "substantive," direct dyestuffs must be long molecules, and the aromatic rings must be capable of assuming a coplanar configuration. Examples are Direct Blue 2B, CI 22610, Direct Blue 6; Direct Black EW, CI 30235, Direct Black 38; Direct Brown 3G0, CI 30045, Direct Brown 1; and many others. A number of direct dyes possessed of free NH_2 groups can be developed on the fiber, thus increasing their insolubility, and hence their fastness to washing. This developing is by the processes of diazotizing the free amino group and then coupling with the developer, which may be β -naphthol. (Shreve, 1967).

Pigment dyes form insoluble compounds or lakes with salts of Ca, Ba, Cr, Al, or phosphomolybdic acid. The dye molecule frequently contains $-\text{OH}$ or SO_3H groups. Such lakes, when ground in oil or other media, form the pigments of many of our paints and inks. In this use class fall such dyes as Lithol Red R, CI 15630, Pigment Red 49; Ponceau 2R, CI 16150, Acid Red 26; Orange II, CI 15510 Acid Orange 7; and the splendid phthalocyanines (pigments). Some basic dyes are used for the tinting of paper in a water-dispersed form of phosphomolybdic (or tungstic) acid lakes. Wallpapers are frequently colored with lakes from basic dyes containing a sulfonic group. Certain insoluble dyes are widely used in apure form, known as toners, or pigment toners, in paints, printing inks, and wallpapers, and especially for the pigment printing method for textiles, employing pigments of metal phthalocyanines and other types. The use of

pigments in the "dope" before spinning rayon, acetate, and synthetic fibers is growing rapidly and is resulting in excellent colors of outstanding all-around fastness. (Shreve, 1967).

Mordant dyes are applied principally to wool, wherein, by the use of a mordant, which may be chromium, or less frequently aluminium or iron, the fastness to light and washing is much increased. Such dyes contain -OH or -COOH radicals frequently attached to azo or anthracene (anthraquinone) complexes. The mordant dyeing is really a metallic salt or lake formed in the fiber. Examples are Alizarin, CI 58000, Mordant Red 22; Chrome Blue Black U, CI 15705, Mordant Black 17; Gallocyanine, CI 51030, Mordant Blue 10; and many others. (Shreve, 1967).

Sulfur, or sulfide, dyes contain a chromophore with sulfur, and are also dyed from a sodium sulfide bath, wherein the sulfur color is reduced to a colorless or light-colored leuco derivative. Sulfur dyes are usually applied on cotton and form a large, low-priced, and useful group, among which we find Sulfur Black, CI 53185, Sulfur Black 1; and analogous dyes, very extensively sold (basis dry weight). These dyes furnish dull shades of good fastness to light, washing, and acids. However, they are very sensitive to bleach or chlorine. (Shreve, 1967).

Vat dyes, including the long-used indigo, are of a chemical structure such that reduction furnishes an alkali-soluble "leuco vat",

with which the fiber, generally of vegetable origin such as cotton, is impregnated. This, upon exposure to air, oxidizes back to the insoluble color. Such dyes are of complicated chemical structure such as indanthrenes, but furnish dyes of exceptional fastness to light, alkaline washing, perspiration, and even chlorine. The vat dyes provide the fast-dyed cotton shirtings and dress goods which, although relatively expensive, are rapidly increasing in use. The vat dyes are likewise made in a paste, with alkaline hydrosulfite-aldehyde reducing agent, printed on the cloth, and passed through an oxidizing bath of sodium bichromate or perborate. Examples are Indigo, CI 73000, Vat Blue GCD, CI 69810, Vat Blue 14; and anthraquinone Vat Jade Green, CI 59825, Vat Green 1. Indigo has a unique and very important use for dyeing wool in extremely heavy (navy blue) shades, where it shows surprisingly good fastness properties. Quite important, also, is the use of several thioindigo dyes for the printing or rayon fabric (mainly woman's dresses) in very bright shades with good fastness properties. (Shreve, 1967).

Solvent, or spirit-soluble, dyes are frequently simple azos or triarylmethane bases or anthraquinones used to color oils, waxes, varnishes, shoe dressings, lipsticks and gasoline. Food dyes are of various structures, selected and tested for harmlessness and employed in coloring foods, candies, confection, and cosmetics. The photographic, medicinal, bacteriological, and indicator dyes are highly specialized products relatively small sales volume but of fundamental importance in the maintenance of our national economy. (Shreve, 1967).

Reactive dyestuffs which link chemically to cellulosic fibers were first marketed in 1956. These represent the first really new class of dyestuffs introduced since the disperse dyes for acetate. The dyes are water soluble compounds which contain reactive groups capable of combining with the hydroxyl groups of cellulose under alkaline condition, establishing a covalent link between the dye and the fiber. The wet-fastness properties of these dyeing is high. (Shreve, 1967).

Fluorescent brightening agents, or "optical brighteners", are used to whiten textiles plastics, paper, soaps, and detergents and to add brightness to delicate dyeings. About \$ 28.4 million worth were sold in 1964, of greatly varying chemical structure. Addition of a good white reflecting pigment like TiO_2 help with paper or plastics. Examples of dyes are derivatives of diamino stilbene, coumarin, etc. (of color Index). (Shreve, 1967).