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# The Principles Of Textile Dyeing

This overview explains the chemical interaction of dye components in various situations.

*By Warren S. Perkins*

Many variables must be controlled in the dyeing of textile materials. To better understand control of variables in the dyeing process, consider the model of a dyeing system shown in Figure 1.

This model describes dyeing as a mass transfer process. The model is applicable to virtually all dyeing systems: continuous or batch; cotton or synthetic fibers; and dyeing of fiber, fabric or garments. The task that must be accomplished in dyeing is the transfer of dye from the dyebath to the fibers in the material being dyed. The depth of color achieved depends mainly on how much dye is added to the fiber.

### Efficient Dyeing

For economic and environmental reasons, a high degree of exhaustion is desirable. Dyes are expensive, and dye that is left in the bath

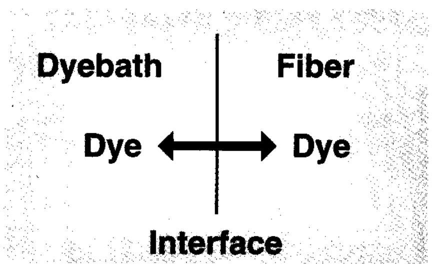


*Figure 1.*

is wasted. Furthermore, dye left in the dyebath is a pollutant that must be controlled and disposed of along with the wastewater from the plant. Often auxiliary chemicals are added to the dyebath to improve exhaustion.

Most dyeing processes are reversible. That is, as dye molecules transfer from the dyebath into the fiber, other dye molecules desorb from the fiber and reenter the dyebath. The amount of dye in the fiber increases with dyeing time until the rates at which dye molecules enter and leave the fiber are equal. When these rates become equal, the amount of dye in the fiber does not change with additional dyeing time. An equilibrium or steady-state condition is established.

Typically, the time required to establish equilibrium is longer than is commercially feasible, so commercial dyeing systems often do not reach equilibrium. If a dyeing is not carried to equilibrium, the exhaustion of dye is less than it would be at equilibrium.

### An Inherent Attraction

Dye distributes between the dyebath and the fiber because it has an inherent attraction for both of these phases. The attraction of dye to the fiber is often referred to as the "affinity" of the dye. Actually, the dye has affinity for both the fiber and the dyebath. The driving force for transfer of a dye molecule from one phase to the other (dyebath to fiber or fiber to dyebath) is the concentration of dye in the two phases. Because dye adsorption is concentration-dependent, the relative amounts of dyebath and fiber used influence the exhaustion.

The term "liquor-to-fiber ratio," or just "liquor ratio," is used to express the relative amounts of dyebath and fiber. The liquor ratio is the amount of dyebath used per unit of material being dyed. If 1 kilogram of dyebath is used per 0.1 kilogram of material being dyed, the liquor ratio is 10 to 1 (10-1). Liquor ratio varies over a wide range depending on the type of dyeing process and equipment used.

*Editor's Note: Warren Perkins is a textile consultant based in Auburn, Ala., and a professor of textile engineering at Auburn University. He was president of the American Association of Textile Chemists and Colorists (AATCC) in 1991-92.*

Values range from as high as 50-1 for some batch processes to as low as 0.3-1 for some continuous processes.

Low liquor ratio, or a smaller amount of bath relative to the amount of fiber being dyed, gives higher dyebath exhaustion (other factors being equal). Therefore, utilization of dye is usually better under lower-liquor-ratio dyeing conditions. Dyeing machinery manufacturers have made great progress in recent years in designing systems to operate at low liquor-to-fiber ratios.

### Interaction Of Components

Fiber, water, dye and dyeing assistants (additives) make up a dyeing system. Each of these four or more components can affect every other component in the system, as illustrated in Figure 2.

The interactions of some of the components in a dyeing system have been studied in detail and are

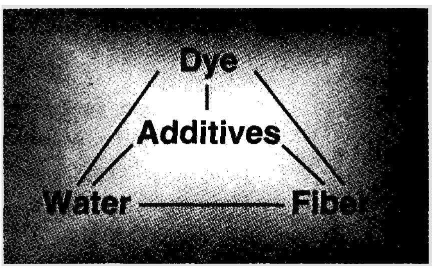


*Figure 2.*

well understood. But sometimes interactions between components are not well understood, and some substances in the dyebath may result in an unpredictable effect.

### Dye/Water Interactions

The two general types of dyes with regard to their behavior in water are ionic dyes and nonionic dyes. Ionic dyes may be either anionic or cationic. In anionic dyes the part of the molecule primarily responsible for color has a negative charge: $Dye^{-}Na^{+}$. In cationic dyes, the colored part of the dye molecule is positively charged: $Dye^{+}Cl^{-}$.

Although the solution formed may be clear and transparent, the dye molecules may be aggregated in water. Degrees of aggregation of dyes can be measured, and aggregation numbers for several dyes have been published. Generally,

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higher dyebath temperature decreases the aggregation number of a dye. Since smaller aggregates should diffuse into fibers more easily, this lower degree of aggregation is one of the reasons cited for the greater dyeing rate observed at higher dyeing temperatures.

Nonionic dyes do not interact strongly with water and are usually used as dispersions in water. Although nonionic dyes are usually thought of as being insoluble in water, they often are slightly soluble. This solubility, although small, may be vital to adsorption and diffusion of dye in the fiber. Nonionic dyes are manufactured to have very small particle size and are formulated with surfactants so they are easily dispersible in water.

### Fiber/Water Interactions

Water is usually the dyeing medium. Interaction between water and the fiber has a major role in application of many types of dyes. Hydrophilic fibers like cotton, rayon and wool attract water. Water molecules diffuse into the amorphous regions of the fiber and break internal hydrogen bonds. Swelling of the fiber results. Swelling of the fiber by water also may be important in dyeing of some of the more hydrophilic synthetic fibers, such as nylon.

Swelling increases the size of openings and increases the mobility of the polymer's molecules in the amorphous regions of the fiber, making possible the diffusion of dye into the fibers. Swelling of the fiber in water is enhanced by higher temperature — another major reason why higher dyeing temperature increases dyeing rate.

Hydrophobic fibers like polyester and some polyamides do not swell much in water. Water plays a less-active role in the dyeing of these fibers. Water still may be needed as the medium to dissolve the dye so that the particles or molecules of dye are small enough to diffuse into the fibrous polymer. Water also may serve as the heat-transfer medium in dyeing of polyester, which often is dyed at temperatures of about 130°C. In continuous dyeing of polyester, water is simply the medium through which dye is deposited on the surface of the fibers and serves no active role in transporting dye into the fibers.

### Dye/Fiber Interactions

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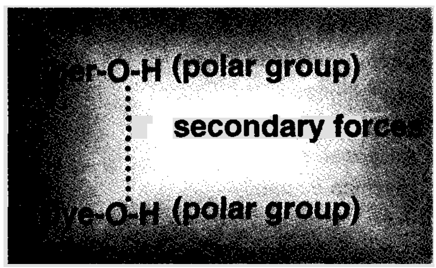


*Figure 3.*

the fiber and is sometimes important in holding the dye in the fiber. Dyes are attracted to fibers because of chemical interactions between the dye molecule and the fiber. The bonding between the dye and fibers may result from weak secondary interactions such as hydrogen bonding or van der Waals forces *(Figure 3)*.

Because each individual secondary bond is relatively weak, multiple interactions between a single dye molecule and the fiber are needed for good bonding to occur. Therefore, dyes that bond to fibers mostly by secondary forces are usually relatively large, high-molecular-weight structures that can have a large area of interaction with a fiber molecule.

$$\text{Dye-SO}_3\text{H} + \text{H}_2\text{N-Fiber} \longrightarrow \text{Dye-SO}_3^- \ \text{H}_3^+\text{N-Fiber}$$

**acidic group** | **basic group** | **salt linkage (ionic bond)**

*Figure 4.*

Diffusion of large molecules in the fiber also is hindered, giving them the potential for better fastness properties than smaller molecules (other factors being equal). Fibers that bond with dyes mainly by secondary forces do not have any specifically identifiable "dye-sites." As a result, there is usually no specific limit to the amount of dye the fibers can absorb. That is, the fiber does not become "saturated" with dye, no matter how much dye is applied.

### Ionic Bonding

Ionic bonding is important in the dyeing of fibers that have strong acidic or basic character. Ionic bonds form between a fiber having acidic groups and a dye having basic groups — for example, acrylic fibers and basic (cationic) dyes. Alternatively, the basic groups can be on the fibers with the acidic groups on the dye — as with nylon fibers and acid dyes. In either case the bonds formed between the dye and fiber are salt linkages and are stronger than the secondary interactions, hydrogen bonds and van der Waals forces, discussed above.

Fibers that bond dyes by forming salt linkages usually absorb only a limited amount of dye, because the dye is attracted to a specific chemical group in the fiber. When these groups (dyesites) are occupied by a dye molecule, they are no longer available to other dye molecules *(Figure 4)*.

Although individual dyes vary greatly, dyes that form salt linkages with the fiber usually have good washfastness characteristics.

### Covalent Bonding

A third type of interaction between dyes and fibers is covalent bonding. Dyes that form covalent bonds with fibers depend on secondary forces for their initial attraction to the fiber. After the dye is adsorbed on or in the fibers, a chemical reaction is induced to cause covalent bond formation between the dye and the fiber. Because the covalent bond is very strong and resistant to cleavage, dyes that form covalent bonds with fibers have excellent washfastness *(Figure 5)*.

Some types of dyes are water-soluble during the application stage but are converted to pigments in the final stages of dyeing. These colorants in their pigment form do not have inherent affinity for the fiber and are simply mechanically trapped in the fiber. Although the fixation mechanism of these dyes on textiles is sometimes described as physical entrapment of dye inside the fiber, the extreme insolubility of the dye in water contributes to the fastness of the color.

It is possible for these dyes to have good washfastness even when the dye is mainly on or near the surface of the fiber. Crockfastness (fastness to rubbing) of pigments deposited on the fiber surface can be poor even though washfastness is good. ❍

$$\text{Dye-X} + \text{HO-Fiber} \longrightarrow \text{Dye-O-Fiber} + \text{HX}$$

**Dye with reactive group** | **Fiber with reactive group** | **Covalent bond**

*Figure 5.*