A Series on Dyeing

Chapter 5: Reactive Dyes and Their Application

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From the year 1856, following Perkin's discovery of the first synthetic dye, the growth of organic chemical knowledge paralleled that of the dye manufacturing industry in particular, and the chemical industry in general. It was explosive! Perkin has even been referred to as "the father of chemical engineering."

By contrast, polymer and fiber chemistries were late bloomers. Viscose rayon fibers appeared ca. 1910 and secondary cellulose acetate fibers ca. 1920. Although both eventually achieved a significant market penetration, neither could ever be called a dominant fiber. The emergence of viscose rayon affected dye manufacturers very little. On the other hand, the arrival of secondary cellulose acetate created waves, and was followed within two or three years by the forerunners of the disperse dyes used today. Although this added a little savor to dye research and development, both continued to be directed primarily towards cotton and, to a lesser extent, wool. It was not until after the second World War, in the early 1950s, that the rapid growth of nylon and polyester began in earnest, and it was decades later before anyone thought it possible that King Cotton might one day be dethroned.

ABSTRACT

This first part of Chapter 5 covers the background to the development of reactive dyes, explains the history which led to their belated discovery and gives the reasons for their present importance. The nature of the dye-fiber bond is covered as well as the processes by which it is formed. The overall procedure for reactive batch dyeing, which involves the three steps of dyeing, fixation and washing-off, is discussed in terms of the chemical and physical interactions involved. Some of the potential problems are indicated, as are possible means by which they might be overcome.

KEY TERMS

Batch Dyeing
Covalent Bonds
Dye-Fiber Bonds
Dye Hydrolysis
Exhaustion
Fixation
Nucleophilic Reactions
Reactive Dyes
Washing-Off
Wetfastness

During the first 50 years following 1856, dye research and development had already discovered members of all but one of the important cellulosic dye application categories known today. After 49 more years the numbers of dyes for cellulose had been extended, performance had been improved, manufacturing and application refinements had been put into practice, but no important new dye application category for cellulose had appeared.

Thus it was with justifiable pride that ICI introduced, in 1956, the first dyes for cellulosics which would actually react with the fiber molecules, to form covalent dye-fiber bonds. The introduction of this new dye application category coincided with the centennial of Perkin's discovery of mauveine.

The General Nature of Reactive Dyes

At this stage, a number of questions may spring to mind. For example: what is special about covalent bonds? What are these reactive dyes? Why did it take so long to discover them? Are they important? Why are they important? Do they match up to the original expectations? These and other such questions will all be addressed, directly and indirectly, in the following sections.

In all dyeing processes dissolved (single) organic molecules or ions (dyes, dye derivatives or precursors) are first adsorbed at the surfaces of the fibers (substrates) and then diffuse into them until they are more or less uniformly distributed throughout. However, once the dyeing process is over, it is necessary that the colors now within the fibers have some degree of resistance to removal by solvents, such as the water which carried the soluble dyes, dye derivatives or precursors out of the dyebath onto and into the fibers in the first place. This requirement may be called wetfastness, and dyes for cellulosic fibers can have a wide range of wetfastness properties. Reactive dyes have generally high wetfastness.

High Wetfastness

Achieving high wetfastness is intrinsically more difficult on the cellulosic fibers because of their extreme hydrophilicity. They love water, and offer little protection against water removal to any soluble chemical species which has diffused inside them. This contrasts with hydrophobic fibers such as polyester. Polyester fibers offer water little opportunity to enter until the temperature is almost up to the atmospheric boil (see a later chapter on disperse dyes).

Dyers and dye chemists have known for a long time that there are only three ways in which dyes can be retained by fibers, and the first two have been used from time immemorial. The three methods are:

- Physical sorption: This relies on the same forces which attracted the dyes to the fibers initially being strong enough to hold onto the dyes through subsequent wet treatments—e.g, with direct dyeings on cellulosic fibers—but also acid, basic and disperse dyeings on other fibers. The wetfastness of direct dyes on cellulose is distinctly limited.
- Mechanical retention: This relies on the formation of insoluble, pigmentary materials out of the soluble chemicals which first diffused into the fibers; e.g., with vat and sulfur dyeings, those of azoic combinations, and also dyeings of mordant and ingrain dyes. None of these offers either a full color range or a very simple application procedure.
- Fiber reaction: Here the dye molecules or ions do not lose all their solubilizing groups after diffusion into the fibers, but in the correct conditions they react and attach themselves by covalent chemical bonds to the much larger fiber molecules, to form new colored derivatives of the fibers. The small number of dye solubilizing groups is totally inadequate to cause the large new dye-fiber molecules to dissolve in water.

Chemical Bonds

Attraction between atoms (bonding), to give molecules or ions, and between the same or different molecules or ions to yield different interaction or reaction products, depends on the movement and distribution of electrical charges, the energy requirements of the process and the stability of the products. The electrical charges represent the probability of finding larger or smaller localized excesses (−) or deficiencies (+) in the distribution of electrons around particular atoms.

For the chemist, the different types of bonds involved in dyeing processes can be discussed in chemical terms *(1)*. Here the treatment will be simple and descriptive only.

- Covalent Bonds: There are two possible extreme cases when considering bonds between atoms. At one extreme lies the covalent bond; e.g., the carbon-hydrogen bonds of most organic chemicals, $\equiv$C-H. In this case, both atoms donate an electron to the bond and the resulting pair of electrons is shared between them. Such bonds share a large amount of energy and it requires even more energy to tear them apart again. Bonds between reactive dyes and cellulose are of this type.
- Ionic Bonds: At the other extreme from the covalent bond lies the ionic bond. In the simplest case, two adjacent atoms may both have an available electron to contribute to a bond, but one atom is able to gain stability by taking them both for itself, thereby gaining an extra electron (negative charge). This will leave the other atom minus one electron (positive charge), which makes it more stable as well. Such is the case with common salt, sodium chloride, which does not exist as covalently bonded molecules, Na-Cl, but as positively charged sodium ions and negatively charged chloride ions, Na^+Cl^-. These oppositely charged ions are attracted to one another electrostatically but can exist independently since nothing is shared (like the opposite poles of two different magnets). Such electrostatic attractions are involved in dyeing with acid and basic dyes (see the appropriate chapter) where fiber molecules can carry charges opposite to those of the dye ions being applied, and because of this, attract them.
- Polarization and Reactivity: It is to be expected that the fairness with which electrons are shared should vary continuously between the sharing of the idealized covalent bond and the "winner takes all" of the ionic bond. Some of the other atoms in covalently bonded organic carbon compounds will always want more than a fair share of the available electrons—e.g., nitrogen, oxygen, fluorine, chlorine and sulfur—whereby they themselves tend to acquire an electronegative character, and their carbon neighbors, an electropositive character. This tendency does not normally lead to ion formation. It is called polarization, and makes individual atoms within a molecule more susceptible to electrostatic interaction with atoms of the opposite characteristic whenever they are in close proximity. Many reactions between different covalently bonded materials are initiated by polarization, and may be completed by formation of products with quite different bonding (electron distribution) than the original reactants. The actual outcome of reactions often depends on complex energy considerations.

Dye-Fiber Reaction: Historical

Reactive dyes are those whose ions or molecules contain groups which are reactive with other groups present in fibers to form covalent dye-fiber bonds. It has been known for many years that wool contains mercapto, amino and hydroxy groups, -SH, $-NH_2$ and -OH, respectively, listed in decreasing order of reactivity, and that cellulosic fibers contain considerable numbers of the latter. It takes two to tango. It is not enough to have a reactive dye molecule. One must also have a reactive group in the fiber.

As early as 1885, Cross & Bevan made yellow and red esters of cellulose by a six-step synthesis. In these products, the dye was covalently bonded to the cellulose and the fastness to washing was excellent; but the reaction conditions were too severe and lengthy to be practical and the fibers were badly degraded (*2,3*).

So, in 1885, the principle was clearly established that chemical, covalent bonding between dye and cellulose could result in dyeings with outstanding wetfastness. But the belief was also reinforced that the hydroxy group of cellulose was of very low reactivity and that reactive dyeing might require to be driven by severe reaction conditions. (Notice the subjectivity of "very low" and "severe": the meaning is in the mind.)

Whether the reasons were conscious or unconscious, for the next 70 years the reaction to form covalent bonds between the more reactive thiols and amino groups in wool and reactive dye species received more attention than that between cellulose hydroxy groups and reactive dyes. The emphasis was placed on reactive dyes for wool despite the fact that improving the already good wetfastness of the dyeings which could be achieved on wool was not a technologically important objective at that time.

Because the first commercial fiber reactive dyes appeared so much more recently than most other important dye application categories, it is worthwhile to point out how complete the scientific and technological documentation is. Not only that, but many of those who worked with reactive dyes since their commercial inception are alive and kicking today, including several of the authors whose work is cited in the references. Even the author of this chapter was an undergraduate intern in the cotton dyeing laboratories of ICI during the summer of 1956.

Properties of Reactive Dyeings

These are almost all that the early researchers could have wished for. They have a full range of bright shades across the spectrum, good to excellent wetfastness with minimal color loss and excellent ratings for the staining of adjacent white goods, with moderate to good lightfastness. They offer all of these advantages, along with great versatility in choice of application methods.

On the other hand, they have moderate tending to poor fastness to chlorine (*2,4*), relatively long batch processing times and high dye and chemical cost. The utilization of color used to be relatively poor, and the waste color going to drain can be easily 30 to 40%, but this deficiency is undergoing serious recent improvements (see later) to perhaps 10% or less in the future. The salt content of the effluent has also been very high, but is rapidly falling with the use of lower liquor ratios in dyeing.

Importance of Reactive Dyes

In 1956, the discovery of reactive dyes was considered so important and their potential utility was so great that all the major dye manufacturers jumped onto the bandwagon as fast as the patent situation would allow. By the end of 1961, BASF, Bayer (now Miles Laboratories in the U.S.), Ciba and Geigy (now Ciba-Geigy), Hoechst (now Hoechst Celanese in the U.S.), Sandoz and Sumitomo had joined ICI in the marketplace with no less than 12 different ranges of reactive dyes between them, representing five different types of reactive groups.

At least eight more ranges of reactive dyes had been introduced by 1988 (*3*), and now, 25 years after their first introduction, the AATCC Buyers Guide (*5*) lists almost 200 different reactive dyes by Colour Index name, representing more than 400 different commercial products.

Currently about one-third of the money spent on dyes for cellulose in the U.S. is spent on reactive dyes;ca. 30% more than for any other class of dyes for any fiber. Several factors might account for some of this value dominance, including high consumption of cotton, consumer demand for bright colors, high wetfastness and most importantly, the high relative cost per pound of reactive dyes. But whichever way you slice it, reactive dyes are very important.

Reactive Dye Sub-Groups

The following will be restricted to these reactive dyes which, when applied to cellulosic fibers, react under mildly alkaline conditions to give covalent bonds between dye and fiber. The restriction is not severe but does eliminate the obligation to discuss the few reactive dyes for other fibers and a few more which were fixed in other ways. This additional information is not hard to find for those interested (*3*).

There is no other class of dyes which has been so fragmented into sub-groups. These are based not only on the relative reactivity of the different ranges of reactive dyes but also on the normal subdivision of dye ranges into groups with similar dyeing performance (as opposed to chemical reactivity) under a particular application condition.

The differences in reactivity results, for the most part, from the incorporation of chemically different reactive groups in the dye molecules. Historically, the most economical reactive groups were inaccessible to many of the different dye manufacturers, and they needed to supply alternatives without running into patent problems. The chemical nature of individual dye molecules also plays a role in determining reactivity, but it is not a dominant one.

The number and ranges of reactivity of these sub-groups are the reasons this chapter will not attempt to provide much specific information on the type and concentrations of alkali and salt, or the preferred application temperatures for individual reactive dye sub-groups. They are also the reasons dyehouses generally stick to one supplier, and why it would be foolhardy to mix reactive dyes from different suppliers unless their compatibility had been clearly demonstrated under the intended conditions of use and, only then, if the reactive groups were known to be the same. However, since many of the early patents have expired, it is now possible to track down comparable competitive dyes. The question is always whether any small resultant savings justify the large potential risks.

The ranges of available reactivities can be illustrated graphically (*3*), but in practical terms it is better illustrated by the results of a batch dyeing study, using model compounds with the same dye molecule substituted by different reactive groups (*2*). The results indicate that very reactive dyes (with dichlorotriazinyl groups, see later) may be dyed at 30C (85F) with amounts of salt and alkali (sodium carbonate) from 25 to 55 and 2 to 15 grams per liter respectively, depending on the liquor ratio and depth of shade. Corresponding figures for dyes of lowest reactivity were 85C (185F), 30 to 100 grams per liter salt and 30 to 50 grams per liter sodium carbonate, although a smaller amount of a stronger alkali would almost certainly be substituted in practice.

Reactive Groups in Cellulose

Chapter 1 (*6*) showed that the cellulose polymer is abundantly supplied with hydroxy groups, -OH, which are themselves relatively unreactive. There are actually three for each repeat unit of the polymer chain. Ignoring the fact that one-third of these hydroxy groups are primary and two-thirds are secondary alcohols, it is convenient to write as a simple representation of cellulose: Cell-OH.

What is generally not appreciated (even by many polymer chemists) is that, in the presence of even dilute alkalis, cellulose behaves as a very weak acid and will ionize according to the normal basic dissociation equation:

$$\text{Cell-OH} + \text{OH}^- \rightleftharpoons \text{Cell-O}^- + \text{H}_2\text{O} \qquad \text{Eq. 1}$$

where

$$[\text{Cell-OH}] \times [\text{OH}^-]_f \div [\text{Cell-O}^-] = K_B \qquad \text{Eq. 2}$$

Eq. 1 is an equilibrium (two-way arrows) in which cellulose plus hydroxide ion (alkali) reacts to give cellulosate anions, Cell-O$^-$, and water.

Eq. 2 indicates that in such a reaction the fraction (cellulose concentration × alkali concentration in the fiber ÷ cellulosate ion concentration), in an excess of water, is a constant, K_B, known as the basic dissociation constant of cellulose.

In work touched on later in this chapter, Sumner (*7*) has been able to calculate the concentrations of cellulosate anions [Cell-O$^-$] and hydroxide ions $[\text{OH}^-]_f$ within cellulosic fibers (the squared brackets indicate concentration, subscript *f* indicates in the fiber and the cellulosate ion could be nowhere else) for any given concentration of chloride ion (from common salt) and hydroxide ion (from alkali) which might be added to the dyebath.

Sumner's work, using the Donnan model of the fiber (see later), made it possible to confirm that the chemical species which reacts with dyes to give dye-fiber bonds is the cellulosate anion, Cell-O$^-$, because the rates of reaction are related to the cellulosate ion concentration and not to the concentration of cellulose. By the same token, it can be shown that the concentrations of hydroxide ions within the fiber $[\text{OH}^-]_f$ and in the dyebath $[\text{OH}^-]_s$ (where subscript *s* means in the solution or dyebath) are also responsible for the rate at which the reactivity of the dye for the fiber is lost, due to the nonfiber reaction of the dye. This undersirable side reaction is called hydrolysis.

The big surprise to chemists was that it does not require extreme alkalinity to generate cellulosate ions, and that these are many times more reactive than cellulose itself.

Since both the cellulosate ions and hydroxide ions are negatively charged, it makes sense that they would be "on the look-out" for areas within molecules which are electron deficient—i.e., positively polarized—with which to react. These include carbon atoms adjacent to nitrogen in the aromatic heterocyclic rings which make up many reactive groups (see later). Such negataively charged species are called nucleophiles; hydroxide and cellulosate ions are nucleophilic reagents.

About This Series

THIS is the eighth installment in this series of papers on dyes and their application. Previous installments have covered the application of anions to nonionic fibers (October 1991), direct dyes (November and December), vat dyes (January and February) and sulfur dyes (March and April). The series is intended to serve as an introductory text and source book for those who want to expand their understanding of the technology of dyeing and coloration. The author, a frequent contributor to TCC and a member of its Editorial Board, is a professor of textile chemistry at Clemson University.

General Dye Features

Reactive dyes have been represented as having as many as five different interlocking features which may be assigned different letters according to the native language or the personal preference of the assignor. The features are: the basic part of the color molecule (C); solubilizing groups (S); bridging groups linking the reactive part of the molecule to the soluble color portion (B); reactive groups (R) and leaving groups (X). This means reactive dyes may be written: S-C-B-R-X. It can be useful to split up the chemical entities primarily responsible for fiber reaction (B, R, X) in this way when it is necessary to emphasize how they individually affect the reactivity (*3*).

Every group, including the bridging, reactive and even the leaving groups, has an effect on the physical properties of the total dye molecule. These include color, molecular size, ability to diffuse into fibers, solubility, substantivity, salt sensitivity, lightfastness, and so on.

However, for general purposes, the author prefers to think of reactive dyes in simpler terms: as water soluble dye molecules with functional substituents; the function being to react with cellulosate ions. For simplicity and convenience in talking about their dyeing reactions, let us identify reactive dye molecules as Dye-X, where the word *Dye* includes all the physical, structural components of a water soluble cellulose reactive dye, except the leaving group X. It will be necessary to deal with the bridging, reactive and leaving groups for the purpose of structure recognition in Chapter 5, Part 2.

All fiber reactive dyes react with nucleophilic reagents, and the overall reactions, regardless of their mechanisms, can be represented by the formula below, where Nu^- is any nucleophilic anion, and X is the leaving group.

$$\text{Dye-X} + Nu^- \rightarrow \text{Dye-Nu} + X^- \qquad \text{Eq.3}$$

Yes, the reactions are more complicated than this, but the equation represents the beginning and ending state of affairs quite reliably. Chemists should refer to Zollinger (*3*) for more complete details.

Batch Dyeing Mechanism

Now that the general introduction to the unique, reactive dye application category has been made, the actual batch dyeing mechanisms can be discussed. The nature of the processes involved, both chemical and physical, will be related to the three steps of conventional reactive batch dyeing (exhaustion, fixation and washing-off), and the possibility of future technology refinements will be explored.

Chemical Processes

The chemical equations which follow are absolutely essential for understanding reactive dyeing:

$$\text{Cell-OH} + OH^- \quad \text{Cell-O}^- + H_2O \qquad \text{Eq. 4}$$

$$\text{Cell-O}^- + \text{DyeX} \xrightarrow{k_R} \text{Dye-O-Cell} + X^- \qquad \text{Eq. 5}$$

$$OH^- + \text{DyeX} \xrightarrow{k_H} \text{Dye-OH} + X^- \qquad \text{Eq. 6}$$

Compare Eqs. 4, 5, and 6 to Eqs. 1 and 3. The reaction represented by Eq. 4 is a reversible equilibrium reaction between cellulose and alkali, to generate the fiber nucleophile with which the dye can react, Cell-O^-. This equilibrium is established almost immediately when the alkali is added to the system.

The reaction represented by Eq. 5 is the key to the formation of the covalent dye-fiber bond and is the reaction, within the fiber, of the dye with the fiber nucleophile, Cell-O^-. This fixation reaction proceeds at a rate determined by the product of the concentrations of the reactants and their intrinsic reactivity, expressed by the rate constant k_R. Squared brackets indicate concentrations; subscripts *f* and *s* mean fiber and solution respectively:

$$\text{Fixation Rate} = [\text{Dye-X}]_f \times [\text{Cell-O}^-] \times k_R \qquad \text{Eq. 7}$$

Table I. Solution and Fiber Phases of Reactive Dyes

Solution (s)		Fiber (f)
Cl^- or $SO_4^{=}$	↔	Cl^- or SO_4
X^-	↔	X^{-a}
OH^-	↔	OH^-
Dye-X	↔	Dye-X[b]
Dye-OH	↔	Dye-OH[b]
Na^+	↔	Na^{+c}
	—	Cell-OH
	—	Cell-O^-
	—	Cell-O-Dye[b]

Notes: [a] X^-, the dye leaving groups, may also be Cl^- or $SO_4^{=}$. [b] Dyes contain anionic SO_3^- groups, so these species are anionic. Dye-X is short lived. [c] Sodium ions from all sources; dyes, salts and alkali.

The reaction represented by Eq. 6 is the hydrolysis reaction, by which reactive dyes are wasted, to form by-products which will no longer react with the fiber. This reaction takes place both in the fiber and in the solution (dyebath) with the same rate constant of hydrolysis, k_H, but at different rates, because the concentrations of the reactants are different in the two locations:

$$\text{In-Fiber Hydrolysis Rate} = [\text{Dye-X}]_f \times [OH^-]_f \times k_H \qquad \text{Eq. 8}$$

$$\text{In-Dyebath Hydrolysis Rate} = [\text{Dye-X}]_s \times [OH^-]_s \times k_H \qquad \text{Eq. 9}$$

The total rate of reaction of the dye, or the rate at which the dye loses its reactivity, is given by the sum of the three rates given in Eqs. 7 through 9. Clearly this is larger than just the rate of fixation (see upcoming section, Dyeing, Step 2: Fixation).

$$\begin{gathered}\text{Total Rate of Reaction} = \\ \text{Fixation Rate (Eq. 7)} + \\ \text{In-Fiber Hydrolysis Rate (Eq. 8)} + \\ \text{In-Dyebath Hydrolysis Rate (Eq. 9)}\end{gathered} \qquad \text{Eq. 10}$$

Physical Processes

Exhaust dyeing reactive dyes on cellulose involves inorganic and dye ions in two phases, liquid and solid, dyebath and fiber. Chemical reactions can take place in the bath or in the fiber, but the physical processes often involve those ions which can move reversibly from dyebath to fiber and back again. Other ions and molecules, particularly cellulose and cellulose derivatives, are not mobile. The situation can be represented in a simple diagram, Table I, which indicates solution and fiber phases, those mobile ions which attempt to equilibrate between dyebath and fiber (double arrows) and the immobile species.

It is no easy matter to scientifically study all these ion movements and equilibria while studying chemical reaction rates as well. The next sections outline a method which is very helpful in such an attempt. The same general approach has proved useful for studying the acid dyeing of nylon and the basic dyeing of acrylics (*7*). However, the next three short sections may be of little interest to dyers.

The Donnan Model: A Research Tool

In science, all sorts of model systems are used. They do not need to be completely realistic, although it helps; however, they need to be useful! The Donnan model of fibers is linked with the name of a pioneer in the area of semi-permeable membranes, and it can be used to examine how the mobile and immobile, reactive and inert, ionic species will equilibrate in dyebath-fiber systems. It is particularly useful for studying the behavior of alkalis, salts and anionic dyes in cellulose-dyebath systems so that the concentration of the different ions in the fiber may be calculated from experimental measurements on the solutions.

The model has been based on a number of assumptions, and it has been used along with a number of constants some of which might be labeled empirical. However, they all have a realistic basis, which means that their use leads to conclusions which make good scientific and practical sense. The assumptions are given below, as are the nature of the constants used to study cellulose. Their values are given elsewhere (*7*).

Donnan Assumptions

The following are Donnan assumptions:

- Cellulose in (textile) wet processes can behave as if the external dyebath or solution phase and the internal or fiber phase are both aqueous liquids, separated by a membrane through which ions but not cellulose (fiber) derivatives may pass; i.e., as if the properties of diffusible ions within the fibers at equilibrium can be confined to a special reservoir of water intimately associated with those outer and inner fiber surfaces accessible to water.
- Electrical neutrality is achieved in both the external (dyebath) and internal (fiber) phases. This means there are equal numbers of positive and negative ionic charges in each individual phase. But the two phases may have different numbers of ions.
- The conditions of Donnan distribution of solutes (such as alkali, salt and dyes) across the membrane are applicable. The most useful condition can be simply stated. At equilibrium, the product of the concentrations of each of the ions of a solute are equal in both the external and internal phases. The only caution needed here is that solutes producing more than two ions, even if two or more are the same, must be treated as if each ion were different. For example, sodium sulfate, Na_2SO_4, ionizes to give three ions, two sodium ions and one sulfate. The product of the concentrations of these three ions is: $[Na^+] \times [Na^+] \times [SO_4^{=}]$ or $[Na^+]^2 \times [SO_4^{=}]$. The same considerations apply

to the sodium salts of anionic dyes which can have four or more sodium ions.

Cellulose Constants

For cellulosic fibers (7) these include the ionic product for water K_W; either the acidic dissociation constant for cellulose, K_A, or the basic dissociation constant, K_B, where $K_B = K_A \div K_W$; the availability of Cell-OH (actually glucose residues) for provision of internal surfaces (41% for cotton, 74% for viscose rayon), which percentages are a function of fiber morphology, crystallinity and amorphous character; the concentration of Cell-OH residues; the concentration of acidic, carboxylate groups in cotton and viscose rayon and the volume of the surface phase in liters per kilogram of fiber (for cotton and viscose rayon: 0.22 and 0.45). These latter values are known as volume terms.

Dyeing

We are now ready to move on to discuss the three principle steps of all reactive dyeing: exhaustion, fixation or reaction and washing-off. A section will be devoted to explaining the significance of graphical representations of the process.

- Step 1: Exhaustion: In conventional processes the required amount of dissolved dye is added to the dyebath at ambient temperature and circulated through the goods. The temperature is gradually raised to the recommended dyeing and fixation temperature and the required amount of salt is added in portions, to exhaust the bath.

This parallels direct dyeing, except in one respect: the substantivity of the reactive dyes is generally quite low, which would require the amount of salt to be high, sometimes as high as 200% owg, or, at a 20:1 liquor ratio, 100 grams per liter. The exhaustion might be quite low, regardless; maybe as low as 10%.

In the next few sections we will see why low exhaustion and high salt concentrations are tolerated. Certainly reactive dyes could be derivatives of selected direct dye molecules with high substantivity (although they are not outstandingly bright in color). Why is this usually not the case?

- Step 2: Fixation: The required (or recommended) amount of alkali is added to the goods with good circulation, and fixation (reaction) proceeds. The hydroxide ion, being a very small ion, enters the cellulose readily and the equilibrium reaction, Eq. 4, the ionization of cellulose, is quickly established. This produces a system with three possibilities for nucleophilic reaction with the dye: two in the fiber (internal) phase, with the cellulosate and hydroxide ions, one in the dyebath, with hydroxide ions.

The dye is distributed between the dyebath and the fiber after Step 1, and reaction proceeds in both phases at rates which are given in Eqs. 7 and 8.

Reaction proceeds until no further increase of color depth takes place on the fiber, at which time there is essentially no free reactive dye left. At the end of this stage, Step 2, there might be a total of anywhere from 75-90% of the color, either exhausted or fixed, on the fiber; i.e., there is 10-25% of hydrolyzed color left in the bath. Of the color on the fiber, 15-25% is not fixed (reacted with the fiber) but is held by substantivity; i.e., only 50-75% of the reactive dye added to the bath initially is covalently bonded to the fiber. The remaining 25-50% of hydrolyzed color will probably end up, along with a high concentration of salt, in the drain.

This state of affairs has satisfied nobody, and in many developed countries it is becoming an environmental liability.

Exhaustion and Fixation Graphs

Steps 1 and 2 can be illustrated graphically; e.g., Fig. 1. This shows the changes in dyebath exhaustion and dye fixation on the fiber, with time, in a conventional dyeing process lasting a nominal two hours, with the alkali addition after 30 minutes. The curves represent the behavior of two commercial dyes from the same sub-group, but with no suggestion that they are suitable for use together. The use of the word *color* on the *y* axis obviates the need to distinguish clearly between Dye-X and Dye-OH, or reactive and hydrolyzed dye.

After 30 minutes, just before alkali addition, Dye I, curve EI, is 46% exhausted, and the majority of the dye at this stage will be in its original reactive form, Dye-X. The shape of the curve seems to indicate that the dye is moderately substantive and could have exhausted to about 60% if the alkali had not been added. The equivalent curve for Dye II, E II, indicates that the original reactive dye, Dye-X, has very little substantivity under the given conditions and has achieved its full exhaustion of about 10% before the addition of alkali.

After the addition of alkali, two new dye species begin to form. Curves FI and FII represent the increase from zero of the covalently bound dyes I and II respectively; Dye-O-Cell. The continuation of curves EI and EII (beyond the 30 minute alkali addition) represent the sum total of all the colored species associated with the fiber. At 30 minutes this color is almost all Dye-X, but Dye-O-Cell and Dye-OH appear gradually, until at t = 120 minutes, it is probably all Dye-O-Cell and Dye-OH. It is not possible to distinguish from the curves alone what percentages of which species of fiber color EI and EII represent.

The figures at the right hand side of the Fig. 1 indicate:

(i) the percentage of the dyes I and II actually fixed: (68%, 66%);

(ii) the percentage of hydrolyzed dyes dropped with the dyebath: (16%, 25%);

(iii) the percentages of hydrolyzed dye exhausted onto the fiber: (16%, 9%);

Together, ii + iii indicate the percentages of wasted color: (32%, 34%).

It is apparent that the increased substantivity of Dye I over that of Dye II has hardly affected the overall yield of fixed dye, but has produced 7% (16% minus 9%) more of a product on the fiber which is moderately substantive and will have to be removed by washing. This is a distinct drawback.

But, how does 66% of Dye II end up fixed, when its substantivity is so low before the addition of alkali? Certainly the added alkali (being an electrolyte, like

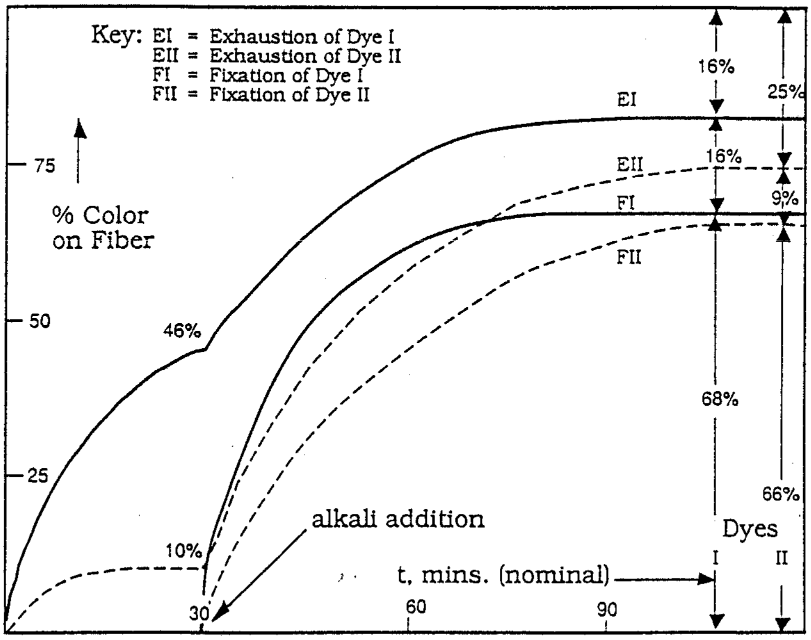

Fig. 1. Exhaustion and fixation *vs.* time for two reactive dyes.

salt) could drive more dye onto the fiber, but surely not seven times as much! The answer lies in the diffusion equilibria. Dye in the bath and dye in the fiber are trying to establish an equilibrium. But every time a dye molecule reacts with the fiber, its place has to be taken by a molecule of dye being transferred out of the bath and into the fiber, in an attempt to re-establish the equilibrium. Even if equilibrium is never reached, there is always a driving force to attract dye out of solution and into the fiber as long as dye continues to react.

- Step 3: Washing Off: The washing off process is lengthy but unavoidable. To achieve the high wetfastness expected from a fiber reactive dyeing, all the hydrolyzed, unfixed dye has to be removed. The more substantive the hydrolyzed dye, the more difficult it will be to remove, and it could continue to bleed slowly over time—c.f. direct dyes—giving unexpectedly poor wash- or wetfastness results.

A batch washing-off sequence might include: a cold water wash at 25 to 60C (75 to 140F); a hot water wash at approximately 60 to 80C (140 to 175F); scouring with anionic surfactant at 80 to 90C (175 to 200F); and all this followed by hot and then cold water washing. The sequence can be critical and manufacturers' recommendations should be followed. Some dyes, notably vinyl sulfone derivatives, can have some of the reactive dye-fiber bonds hydrolyzed if the first process is carried out too hot, with consequent color loss. All dye-fiber bonds are capable of being hydrolyzed under severe enough conditions of temperature and at too high or too low pH's. Vinyl sulfone derivatives are more sensitive on the alkaline side; heterocyclic carbon-nitrogen derivatives are more sensitive on the acid side. For the structures of those reactive species, see Chapter 5, Part 2.

Hydrolysis and washing have been discussed at length (*2,3*), and the danger of too severe washing producing acidic internal fiber pH's and dye hydrolysis is real (*7*). The economics of washing have also been examined (*8*).

A good test for whether all the hydrolyzed dye has been removed, or, for the effectiveness of the washing procedure, is the so-called Hot-Wet Press test. A sample of the dyed goods is sandwiched between layers of bleached cotton fabric and heated with a hand iron or a hot head press for about 15 seconds. Any loose color in water migrates towards the heating surfaces and is transferred to the white cotton fabric. A stain generally indicates unsatisfactory washing-off, although for some heavy shades no process will be adequate. If the goods are not to be resin finished, there may be no alternative other than to resort to cationic fixatives. This may lead to lowered lightfastness and is not preferable to a good washing-off.

Process Improvement

What can be done to reduce the amount of hydrolyzed dye and increase the amount of dye covalently bonded to the fiber? This question can be expressed in chemical terms by examination of Eqs. 7, 8 and 9.

How can one: (a) increase the ratio k_R/k_H, i.e., make the fixation (reaction) rate constant higher relative to the hydrolysis rate constant, Eqs. 7, 8 and 9; (b) increase the fraction $[\text{Cell-O}^-]_f \div [\text{OH}^-]_f$, also with a view of making the fixation reaction proceed faster relative to hydrolysis, Eqs. 7 and 8; and (c) reduce the value of $[\text{Dye-X}]_s \times [\text{OH}^-]_s$, i.e., reduce the exposure of dye molecules in solution to hydroxide ions in solution, Eq. 9, by reducing either or both?

Viewed from these three angles the problem looks very difficult.

- First, the ratio of k_R/k_H is a property of individual dye molecules and is out of the hands of the dyer.
- Second, provided the pH is kept below 11, increasing the salt concentration can raise the value of (b) $[\text{Cell-O}^-]_f \div [\text{OH}^-]_f$. However, the amount of salt suggested by the manufacturer is usually the optimum for the particular procedure. So there is not much help here either.
- Finally, the traditional batch dyeing method, of salting of the dye and only then adding alkali, should have taken care of the hydrolysis of dye in solution, Eq. 9. Certainly the dye in solution could be reduced to very little before the alkali addition if substantive direct dye structures were used. But the problems of wash-off would be a serious drawback. Alternatively, increasing the substantivity of existing dyes by increasing the recommended salt additions or lowering the recommended temperature might be effective were it not for the adverse possibilities. Salt addition may decrease the rate of dye diffusion and increase the possibility of dye aggregation, even induce precipitation, while adding to the effluent problem. Lowering the temperature would slow the rate of dyeing.

There are some benefits from lowering the liquor ratios, which would increase substantivity, although the salt may have to be reduced to avoid aggregation or solubility problems.

Surely lowering the liquor ratio is not the only possibility? This question will be addressed in the section on Dyestuff Research.

Review

Some aspects of reactive dyeing should be repeatedly emphasized:

- Whenever several dyes are used together to match a particular shade they should have been selected with similar dyeing and fixation characteristics (compatibility) in mind. In the conditions of application they should not only be adsorbed at similar rates and to similar extents, but they should also react at similar rates. In general, this means that they should come from a set of dyes with the same fiber reactive group(s).
- Once an appropriate dyeing recipe has been determined, the process variables of time, temperature, salt, alkali and liquor ratio should all be controlled as carefully as possible to ensure the optimum shade reproducibility and dye fixation.

It is safe to say that unless these conditions are fulfilled, the results will not always be up to expectations.

The traditional independence of the dyer, to be flexible with formulations and procedures, is seriously challenged by the reactive dyes. Many of the tools needed to fine tune the dyeing properties and procedures for the different groups of reactive dyes depend on chemistry, and are in the hands of the dye manufacturers. The market demand for bright colors of high wetfastness has put reactive dyes in a prominent position which seems likely to be reinforced in the future—so this situation is unlikely to go away.

There is no virtue in fighting what cannot be changed, so the dyer must learn to accept reactive dyes for what they can do for him, not fight against what they will not permit him to do. But first he should carefully select the supplier, or suppliers, most likely to be responsive to his present and future needs.

Many reactive dyes have drawbacks which will demand the attention of chemists. The overall percentage fixation of the early reactive dyes is low compared with that expected from other dye categories. The result is that the effluent is high on both waste (hydrolyzed) dye and salt. Furthermore, the color yield of many reactive dyes can be quite sensitive to relatively small changes in the application conditions. These problems, lying between dye manufacture and the dyed goods market, are waiting to be solved.

Research groups of some dye manufacturers are pursuing these problems with vigor.

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