

Chapter 8: Disperse Dyes and Their Application to Polyester

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DISPERSE dyes are nonionic, have very limited solubility in water at room temperature and have substantivity for one or more hydrophobic fibers; e.g., polyesters and nylons. They are usually applied from a fine aqueous dispersion containing some dissolved dye. This definition changes the emphasis of that given in the Colour Index (1) to stress the most important fibers and to reflect the fact that it is the aqueous solution from which dyeing normally takes place, despite the low water solubility of the dye.

Solutions are characterized by the presence of the solute (dye) as single molecules; i.e., in a monomolecular form. Even in thermofixation and heat transfer printing (2), where dyeing takes place in the absence of water, the dyes must first sublime into single molecules (dissolve) in air before diffusion into the fiber can take place.

The AATCC Buyer's Guide (3) lists over 700 disperse dye products under more than 200 Colour Index names. The majority of these are blues, ca. 30%; reds, ca. 25% and yellows, ca. 20%. Oranges and violets both account for ca. 8% and browns account for ca. 3%. This leaves little room

for blacks and greens but in no way indicates a problem in obtaining black and green dyeings with disperse dyes; the color gamut obtainable is extremely large. It does reflect the difficulty of synthesizing green and black compounds, which are nonionic and of small enough molecular size (relative molecular mass, rmm) to have substantivity for and to be able to diffuse into hydrophobic fibers.

C.I. Disperse Blacks 9 and 33 are actually navies which only become blacks after they have been diazotized and developed (cf. the aftertreatment of direct dyes, Chapter 2 and azoic combinations, Chapter 6). But black disperse product mixtures are readily available, and they are almost invariably mixtures of a navy blue shaded with appropriate proportions of a red or rubine plus a yellow, yellow-brown or orange component. Because they have more than one principal chemical component, they cannot have a C.I. name.

There is also no particular problem in obtaining a wide variety of green shades with disperse dyes, even though only one green disperse dye, C.I. Disperse Green 9, is listed (3). But the choice of blue and yellow components is in the hands of the user. Green disperse dye mixtures are not generally available.

Disperse Dye Classification

Dyes may be classified in a variety of ways, some of which are unique to the particular application category. Disperse dyes are no exception. As might be anticipated, chemical classification by chromophore is generally the least useful to the dyer. However, there are some chemical differences between disperse dyes which affect their performance in dyeing. These include the ease with which they are reduced and the ease with which they are hydrolyzed.

Reduction Clearing

Because disperse dyes have such limited solubility in water, some particulate disperse dye may still be occluded on fiber surfaces after the dyeing phase is complete. If this condition is suspected, the last stage of the dyeing process may need to be one where surface dye is removed. Adverse results of excess dye on the fiber surfaces include considerably reduced wetfastness, washfastness, sublimation and drycleaning fastness, as well as dulling of the shade.

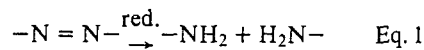
With experience, the presence of exces-

sive amounts of surface dye can be determined by simply agitating a sample of the dyed goods in a little cold acetone for a few seconds, when surface dye will dissolve. The acetone will not extract dye from within the fiber, which remains unswollen, but will dissolve surface color.

The usual practical procedure for removing this unwanted dye is called reduction clearing and uses a bath of about two grams per liter of both caustic soda and sodium dithionite (hydro), as 100% solid products, plus about one gram per liter of a stable surfactant.

A treatment for 20 minutes at ca. 70C (160F) is often sufficient to clear the fiber surfaces, but the ease of removal varies from chromophore to chromophore and dye to dye. Provided the clearing temperature is not above the dyeing transition temperature, no dye will be stripped from within the polyester fibers.

The largest majority of disperse dyes contain the azo group, $-N=N-$. This group is easily split into two amino groups by treatment with reducing agent:



which makes them particularly suitable for reduction clearing since the amino residues are virtually colorless unless deliberately oxidized to form totally different products.

Some bulky azo dye molecules, notably the navies as a group, are so sensitive to reduction that under conditions of too high pH they can cleave at the azo group, even during the dyeing process, to give dyeings of a characteristic lighter, duller and greener appearance. The condition is more pronounced in polyester/cotton blends.

Another chromophore still found in some of the brighter blue, pink and red disperse dyes, despite its cost, is anthraquinone. This is more difficult to reduce and is not destroyed during normal reductive clearing. However, as in the case of vat dyes, the anthraquinone residue is at least partially and reversibly reduced to a soluble sodium leuco form which can be washed away but which on subsequent exposure to air becomes insoluble again.

Hydrolysis of Dye Esters

Another chemical group frequently found in disperse dyes is an ester group, often an acetyl group, $-O-CO-CH_3$, and like the

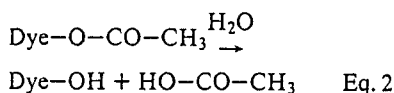
ABSTRACT

The fiber, dye and dyebath variables which affect the batch dyeing of polyester with disperse dyes are discussed, as are some of the chemical properties of disperse dyes which influence the normal conditions of dye application, stripping and reduction clearing. Discussion of the continuous dyeing of polyester is deferred to a later chapter on dyeing polyester/cellulosic fiber blends.

KEY TERMS

Batch Dyeing
Disperse Dyes
Dye Classification
Fastness Properties
Glass Transition Temperature
Heatsetting
Microfibers
Oligomers
Polyester
Trimers

acetyl groups in cellulose acetate it is susceptible to hydrolysis in neutral and alkaline conditions:

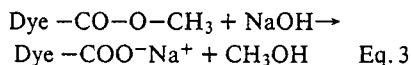


The products are acetic acid and a different azo disperse dye whose color may be quite different from that of the parent dye. Usually the wavelength of maximum light absorption (minimum reflectance) is shifted to a longer wavelength. This is known as a bathochromic shift, in which colors change in the general direction: yellow→orange→red→violet→blue→green. The subject will be discussed more fully in a section on color and constitution. However, two additional, widely different points are worth noting here.

The presence of hydrolyzable groups in many disperse dyes and their protection is the principle reason dyeings are generally made on the slightly acid side. The pH has no fundamental role in the dyeing mechanism as such and some disperse dyes without ester groups do not need a weakly acidic dyebath.

Dyes and dyeings in any application category have traditionally been presented—e.g., in shade cards, the Colour Index (1) and until recently in the Buyer's Guide (3)—in the same bathochromic series order listed above. Blacks are shown last and browns (being dull oranges) are sometimes presented after orange and sometimes between green and black. To simplify processing by computer, the Buyer's Guide now lists dyes alphabetically by color—i.e., black, blue, brown, green, orange, red, violet and yellow—and the Colour Index is considering the possibility of doing the same. While it makes no coloristic sense, the alphabetical system simplifies the processing of the data.

A group of disperse dyes utilizes the alkaline hydrolysis of esters in an ingenious way. These products contain ester groups in the reverse orientation relative to the dye chromophore to that shown in Eq. 2. During alkaline scouring, without the need for a reducing agent, the ester link is hydrolyzed, the surface dye becomes a water soluble carboxylate salt and is easily removed by washing.



Energy Level

Most disperse dye classifications are based on some form of generalized grouping according to their rates of dyeing and resistance to sublimation. For example, a major company in the United Kingdom has chosen to classify its disperse dyes into four groups, A-D, where subgroup A contains those dyes with the highest rate of dyeing on polyester and the lowest subli-

mation fastness, while the dyes in subgroup D are just the reverse (4, 5).

The fact of the matter is that the relative dyeing, physical and most fastness properties of disperse dyes lie scattered around a line from generally small molecules (low rmm) with low polarity, poor heat and sublimation resistance, rapid rates of dyeing and good leveling characteristics to generally much larger molecules (high rmm, but still not very large as dye molecules go) which are quite polar without being ionic, with good heat and sublimation fastness, poor leveling and low rates of dyeing. Note that lightfastness is not a property which is dependent on the molecular size or polarity.

A disperse dye's suitability for dyeing cellulose acetate, carrier dyeing polyester, high temperature dyeing of polyester and dyeing of polyester/cotton blends by thermofixation runs along the same line from A to D. But the precise position of an individual dye relative to others on the line depends on the particular physical property selected and therefore any subdivision is somewhat arbitrary.

In the U.S. it is normal to classify disperse dyes into three subgroups called low, medium and high energy (L, M and H). These cover the same range of properties as the A-D classification mentioned earlier. Again the groups are somewhat arbitrary. But disperse dyes within any one of the subgroups are much more likely to have similar dyeing and fastness characteristics (other than lightfastness) and are consequently more suitable for dyeing together than dyes outside the same subgroup. Because of the number of available dyes, there is still plenty of room for selecting dyes within any subgroup which can deliver the particular characteristics desirable in the final dyed product.

As an illustration, one major manufacturer carries a line of just over 30 disperse dyes principally for polyester. About 25%

are low energy dyes. Six are very suitable for carrier dyeing, a different six are very suitable for high temperature dyeing and only one is very suitable for dyeing the polyester in polyester/cotton blends by thermofixation. About 25% are medium energy dyes. Three are recommended for carrier dyeing, nine are very suitable for high temperature dyeing and five are very suitable for thermofixation. Nearly 50% are high energy dyes. Only one is recommended for carrier dyeing, four for high temperature dyeing and 11 for thermofixation.

Fastness Properties on Polyester

The fastness properties of disperse dyes on polyester cover a wide enough range for an adequate dye selection for most end uses. The same dyes generally show poorer fastness on nylon (see later).

Lightfastness ratings at the ISO standard depth (1/1 SD) can easily be in the 6-7 range on the Blue Wool Scale of 1-8, although they do drop slightly if the light source is a carbon arc as opposed to xenon lamp. As the depth of shade decreases, lightfastness drops, a phenomenon shared by dyeings of all application classes of dyes.

If extremely high lightfastness is needed (automotive fabrics), a nonionic UV inhibitor may be added to the dyebath and applied to the fiber along with the dye. These compounds, often benzotriazoles, work much like sunscreen, screening out and dissipating UV radiation to prevent sunburn.

Wetfastness tests are frequently conducted after the goods have been reduction cleared and heat set; e.g., at 180C (356F) for 30 seconds. They are assessed in terms of the staining on multifiber or adjacent nylon piece goods. Ratings of 4+ out of 5 are readily achieved on regular denier fibers. What is interesting here is that the ratings are very dependent on the extent of clearing of the fiber surfaces, the duration and temperature of the heat treatment and whether the fabric has been treated with a finish of any kind. Heating disperse dyed goods causes the dyes to tend to migrate towards the fiber surfaces and some of the disperse dyes are quite soluble in hydrophobic surface films; e.g., in softeners which may have been applied. Fastness to crocking or rubbing as well as drycleaning suffers if dye migrates to the fiber surface or surface layer.

For those dealing in imports and exports of dyed goods, it is vitally important to be aware that the methods of fastness testing, and consequently the ratings for dyed goods, vary from country to country. The International Organization for Standardization (ISO) has developed a series of fastness tests which are often very different from test methods (6) used in the U.S. Söll (7) compared tests for 30 fastness properties as run in 22 countries. The U.S.

About This Series

THIS is the fourteenth 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), sulfur dyes (March and April), reactive dyes (May and June), azoic combinations (August and September) and the application of nonionic dyes to fibers (October and November). 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.

Disperse Dyes

methods were essentially the same as the ISO SN105 methods in only 7 of 30 cases, somewhat similar in 13 of 30 cases and not comparable in 10 of 30 cases. The moral is do not buy or sell to colorfastness or any other specifications you do not understand.

Disperse Dye Application: General

At a rough estimate, refs. (5) and (8) devote the equivalent of about 100 pages of this magazine to the many different aspects of dyeing man-made fibers with disperse dyes. To illustrate the technical depth of coverage, 43 pages deal with the variety of textile forms in which polyester can be dyed and the special precautions necessary for their handling.

Here, a general treatment will be given which is appropriate for fulfilling the present need (9).

Of course, a great deal more is now known about the detailed physical properties of polymers in general, fibrous polymers in particular, than was known when synthetic fibers were introduced 50 years ago.

The importance of fiber morphology—the particular arrangement of polymer molecules within fibers—was quickly appreciated. The general orientation of the polymer molecules, the extent to which segments of the molecules were physically bound to those of adjacent molecules to give crystalline areas, the extent to which other segments were free to move as if in an amorphous viscous liquid, how much of the fiber was actually unoccupied by polymer molecules (free volume) and other considerations, such as the size and distribution of the crystalline and amorphous areas, have all been studied extensively (10).

As a result, a quasi-quantitative picture can be drawn to show, for example, why polyester fibers cannot be readily dyed in the absence of either high temperatures or carriers, or why heat, tension and other influences such as the addition of different comonomers affect the dyeing properties of nylon and polyester fibers.

It is interesting to note that by far the most sensitive of all available methods for detecting subtle difference between fibers, or changes in fibers, is still competitive dyeing (10). Unfortunately for fiber physicists, competitive dyeings will not reveal precisely what these subtle morphological differences are, only that they are present.

Disperse Dyeing of Polyester

Subsequent papers in this series will deal with application and application related topics more specifically related to fibers—polyester, nylon and secondary cellulose acetate—in order of their importance

relative to disperse dyeing. The first group of topics will therefore be related to polyester.

Polyester Fiber Physical Factors

The next few sections will deal briefly with those factors which affect the accessibility and the availability of polyester fibers towards disperse dyes. Fiber accessibility differences influence the rate of dyeing, particularly in the early stages; fiber availability differences influence the extent of dyeing which can be achieved at equilibrium. Both can contribute to barré or barness (Chapter 7). The former is the more usual cause of dyeing problems and is fortunately easier to overcome.

Drawing

Undrawn and partially oriented yarns (POY) can be dyed quite readily since the fiber molecules have not yet been well oriented. After drawing the molecules become much better aligned in the fiber direction, and as the draw ratio increases, the rate of dyeing or fiber accessibility decreases. The fiber availability does not change much in drawing until one reaches the high draw ratios of industrial yarns.

Accessibility differences between fibers can be overcome provided that the dyes being used and the conditions of dyeing are conducive to leveling in the diffusion and equilibration stages of dyeing which follow the initial differential strike.

Heatsetting and Tension

There is no doubt that polyester fibers and filaments alone, in yarns or in polyester woven or knit fabrics, are morphologically changed during heatsetting. If this were not the case, there would be no virtue in heatsetting. The resulting heatset products can be expected to dye at different rates than the original fibers.

It is hard to be definite about the magnitude of the effects to be anticipated in practice for they vary, not only with the temperature and duration of the heatsetting but also on the conditions of tension in which the goods are held. If fabrics are used, the fully relaxed, natural dimensions of the fabrics affect the tension conditions. Even the individual dyes used can influence the results.

The work of Marvin (4) showed that pieces of a filament polyester fabric held to constant dimensions and heatset at temperature intervals between 120-230C (248-446F) dyed to different depths when dyed with 2% owg C.I. Disperse Red 1 for 90 minutes at the boil without a carrier. Under these conditions dyeing was not complete, equilibrium exhaustion was not achieved and the percentages exhaustion, from dyebaths containing the differently heatset goods, reflect the changes in the relative rates of dyeing.

Fabric set at 120C showed 53% exhaustion, which fell to minimum values of

about 34% exhaustion at heatsetting temperatures between 150-190C (302-374F), rising rapidly to 75% at 230C. If the fabrics had been allowed to relax the minimum would have tended to rise.

Glass Transition Temperature, T_g

Polyester fibers are intrinsically slow dyeing at the boil. Below 70-80C (158-176F) they are for all practical purposes undyeable. This leaves only 20-30C in which the rate of diffusion can increase before the atmospheric boil is reached.

Even though the rate of dye diffusion increases very rapidly, even exponentially, above this 70-80C temperature range, few dyes will diffuse fast enough at the boil to reach exhaustion during a normal dyeing time if no carrier is present.

The temperature above which polyester dyeing begins to occur more rapidly has been called the dyeing transition temperature. This temperature is reduced when a carrier is present and may even be affected by some of the dye molecules themselves. It cannot be just coincidence that this temperature closely corresponds to a more fundamental physical property of polymers known as the second order or glass transition temperature, T_g, which can be measured quite independently.

The glass transition temperature is the temperature at which the moveable segments of the polymer chains become quite suddenly susceptible to deformation and displacement, the polymer properties change from glassy to rubbery and in the increasing thermal agitation of the polymer segments, the dye molecules can grasp the opportunity to slip between them into the body of the fiber.

Fiber Structure Modification

The inclusion of alternative co-monomers into regular polyester (mentioned in Chapter 7), apart from offering the possibility of making the fiber dyeable with cationic dyes, has the effect of lowering both the melting point of the fiber and also its glass transition temperature. The effect can be attributed to the new monomer disrupting the molecular orderliness of the structure, making it easier to leave the glassy state. The same effect can be achieved with the introduction of other nondiffusible, large molecules into the polymer.

Fiber manufacturers have devoted much time and effort in attempts to find new polyester fibers which retain all the desirable characteristics of the present products while adding disperse dyeability at the boil, without carrier, for dyes of high enough energy level to have outstanding heat and sublimation fastness. The target remains elusive. One of the problems is the deterioration of some of the physical characteristics of the fiber with the lowering of the glass transition temperature. Another is cost.

Fiber Fineness

Much attention has been given recently (11) to dyeing microfibers. These are fibers with fineness of less than one decitex (dtex); i.e., fibers for which 10,000 meters would weigh less than a gram. One decitex equals 0.9 denier. It is important to appreciate that the division between micro and regular fibers is quite arbitrary. Wool dyers have been making allowances for differences in fiber fineness for more than 50 years. It is also important to note that these are not microdenier fibers, a misnomer which relates to fibers of fineness ca. 10^{-6} denier.

What has changed is that man-made fibers can now be made substantially finer than the finest natural fibers and that the magnitude of the differences in fineness possible between micro and regular man-made fibers, and which might confront a dyer, is much greater than it has ever been. This means that dyers will not simply need to adjust dye formulations slightly to compensate for fibers of different dtex, but they will need to make adjustments which could be several hundred percent in the amounts of dye used to achieve the same apparent depth of shade.

A useful preliminary relationship between the percentages of dye on weight of goods (C) needed to achieve a particular depth of shade on polyester fibers of two different finenesses (dtex) is given below:

$$C_m/C_r = (\text{dtex}_r/\text{dtex}_m)^n \quad \text{Eq. 4}$$

Here subscripts m and r can be used to indicate micro and regular fibers but could also be used to designate any two fibers of different fineness (denier, dtex). The value of n is normally taken to be 0.5, which means the right hand term of Eq. 4 is the square root of $\text{dtex}_r/\text{dtex}_m$.

Putting arbitrary values for dtex_r (4.5) and dtex_m (0.5) into Eq. 4, gives:

$$C_m/C_r = (4.5/0.5)^{0.5} = \sqrt{9} = 3$$

It takes about three times as much dye to dye this microfiber to the same apparent depth as the regular fiber. Unfortunately, the relationship may not be exact, and in any case was only intended to apply (12) when all other fiber characteristics are identical; e.g., cross section, surface character, delustrant percentage, morphology. The structure of the yarn or fabric in which the fiber is used must also be held constant for the relationship to apply. Also, dye penetration must be uniform for Eq. 4 to apply.

Such marked denier differences can affect dyers in a number of ways, using the example above as an illustration.

- As seen already, the microfiber will need approximately three times as much dye to achieve the same apparent depth of shade (cf. Eq. 4).

- The microfiber will dye approximately three times as fast which could lead to the need for procedural changes in dyeing to

counter possible unevenness due to inadequate circulation, particularly in pale shades. The dyeing rate increases because an equal weight of the microfiber will have three times the surface area.

- If the same apparent depth is dyed on both fibers, the wetfastness after heatsetting of the shade on the microfiber will be significantly reduced. This is because of both the increased surface area and the greater percentage dye on the fiber.

- The lightfastness of the dyed microfiber will be significantly reduced at equal apparent depth.

- Problems in uniformity when dyeing polyester microfiber fabrics could result from difficulties in keeping the fabrics properly wetted. The closeness of fiber packing possible with polyester microfiber fabrics makes them very suitable for rain-wear applications since the fibers are so difficult to wet.

Polyester Dyeing Procedures: General

The continuous pad-thermofix process, which is of such enormous importance in dyeing polyester/cellulosic fiber blended fabrics, has proved unsuitable for all but narrow fabrics of 100% polyester, such as seatbelts and ribbons. The process can be used for sliver and continuous filament tows, but these are not major factors in the U.S. Consequently, the polyester dyeing procedures considered here will be batch procedures and further consideration of thermofixation will be deferred until the chapter on blended fibers and fabrics.

Preparation

Besides the dyeing procedures there are several other processes involved in the production of dyed polyester goods. The first of these is preparation—a scouring and cleaning process.

Polyester fibers can be dyed in a variety of physical forms anywhere in the chain from fiber to greige goods. Not all possible forms need a preparative step prior to dyeing. Loose stock or raw stock will have received only small amounts of applied processing aids, most of which should be self emulsifiable. Such products may be loaded directly into the dyebath although it might be desirable to give them a water rinse before doing so.

On the other hand, knitgoods might be heavily oiled, yarns may be waxed and woven goods may contain sizing materials, all of which should be removed prior to dyeing. Any cationic materials applied during processing must be removed, since they will interfere with the anionic surfactants essential to insure good dye dispersions.

A simple anionic surfactant plus soda ash scour, with about two grams per liter of each component in a lukewarm bath [40-50C (100-120F)], will often be satisfactory.

Sized goods will need an appropriate

desizing, and heavily oiled or waxed goods may even require scouring in the presence of a solvent emulsion to be followed by rinsing.

Problems should not arise unless the goods are contaminated by locally heavy stains. It is important to be sure that no residual fiber lubricants are carried over to contaminate the dyebath. In this same regard the use of solvent or surfactant-containing spotting agents should be avoided.

Batch Dyeing Procedures

In general, batch dyeing procedures divide naturally into those conducted at the boil in the presence of up to 10% owg of carrier and those conducted at temperatures above the boil in pressurized high temperature (HT) dyeing equipment. The HT procedures may be run with or without carrier. The choice of equipment will depend on its availability and the nature of the goods to be dyed.

The liquor ratio will be determined to a large extent by the equipment to be used. It could be as high 20-30:1 for becks, 5-10:1 for jet dyeing machines and 3-5:1 for package dyeing machines. Continuous padding applications use even less liquor, 0.6-2:1.

The point of departure chosen here is a conservative, generalized procedure for dyeing piece goods in a jet dyeing machine at 20:1 liquor:goods ratio. A typical standard HT dyeing method might include $x\%$ disperse dye(s) owg; a suitable pH buffering system to control pH to 4.5-5.5, (e.g., 1 gram per liter ammonium sulfate adjusted, with the bath at full volume, to pH 4.5-5.5 with formic acid); and about 0.5 grams per liter of a suitable anionic dispersing agent. Alternatively, acetic acid is frequently used to adjust the pH without the addition of ammonium sulfate, although this is not a true buffer system.

The dyes are dispersed separately in water and added to a bath at about 50-60C (120-140F) containing the ammonium sulfate, the dispersing agent and the goods.

The pH is adjusted to 5-6 with formic acid and the liquor level to 20:1, while the temperature is raised to 70C (158F) and the dye liquor is circulated through the goods. This temperature is still below the glass transition temperature and no dyeing will have taken place.

With good circulation, the bath temperature is raised to 130C (266F) at 1.5C (3F) per minute and held there for 60 minutes. The dyebath is then dropped at as high a temperature rate as possible.

The goods are rinsed and given a reduction clear in a bath containing the equivalent of two grams per liter of both 100% solid caustic soda (sodium hydroxide) and hydro (sodium hydrosulfite, properly known as sodium dithionite) at 70C for 20

minutes. The last steps in the procedure are rinsing and neutralization.

The process outline is similar to the one given by Schuler (13) except that he used an atmospheric dyeing with carrier as an example. The last decade has seen carrier use in most highly developed countries fall dramatically for obvious environmental reasons. However, in some small commission dyehouses, in garment dyehouses and in some principally cotton goods and single knitgoods dyehouses, the cost of purchasing pressure dyeing equipment is still considered prohibitive and a rear guard action is being fought against the elimination of carriers.

High Temperature Procedure

The components of the high temperature procedure will now be examined in detail to find the purpose of every chemical and every step, in order to be able to modify the procedure on demand for the purpose of fitting it to any given set of circumstances.

Water

There is no category of dyes for which water quality is unimportant. Traces of soluble copper and iron salts can affect the shade of some disperse dyes quite markedly due to the formation of co-ordination complexes. The presence of calcium and magnesium cations can interfere with the anionic dye dispersing agents or anionic leveling and wetting agents present in the dyebaths. For these reasons, small amounts of chelants might be routinely added to disperse dyebaths, particularly when problem dyes must be used.

The effect of pH on some dyes has been mentioned earlier. Ideally pH should be buffered in the range of 4.5-5.5 to minimize the possibility of dye hydrolysis.

Surfactants

There are a multitude of purposes for which surface active agents are added to dyebaths. They include the wetting, penetrating and de-aerating of the goods to ensure that there is intimate, uninterrupted contact between the dyebath and all the fiber surfaces. Since the terms wetting, penetrating and de-aerating are essentially synonymous, there is no need for more than one auxiliary product to fulfill these demands. Such products are normally anionic surfactants. Anionic surfactants are also used to stabilize the diluted dispersions of the dye. This is necessary particularly when dyeing paler shades where the dyebath concentration of surfactant introduced with the dye itself would be small.

The levelness of the dyeing can be improved by controlling the rate of exchange of dye from the dyebath to the fiber. This is the function of other generally nonionic surfactants which are selected for their ability to form surfactant micelles attractive to the dye. These can be

thought of as competing with the fiber for the dye, thus slowing down the rate at which the dye would become available to the fiber. They are called leveling agents, or perhaps more correctly, retarders.

All surfactants can generate considerable foam, except when they are formulated from intrinsically low foaming materials, or when they include defoaming agents for the purpose. Although silicone derivatives are wonderfully efficient defoamers, they are capable of forming water resistant spots on the fiber surfaces if there is any cracking of the emulsions. Their use is to be avoided where practicable.

Temperature and Time

Hypothetically the time and temperature parameters could be optimized for each individual machine, dyebath formulation and type of goods. Practically speaking, such detailed optimization is often out of the question. However, it is still worthwhile to remember that the most cost effective choice of starting temperature, rate of temperature rise, dyeing temperature and length of dyeing which will produce a well exhausted dyebath, with goods of satisfactory color uniformity and shade consistency batch to batch, can mean the difference between a healthy and a marginal operation. A general rule of thumb has the starting temperature about 70-80C (160-180F), the rate of temperature rise at 1.5-2C (3-4F) per minute, the dyeing temperature between 115-130C (240-265F) and the time of dyeing at temperature from 15-60 minutes. Note the absence of a carrier or atmospheric dyeing recommendation.

The conditions should be chosen such that not more than 2-3% of the dye is exhausted for each full cycle of goods through the dyebath or dyebath through the goods. This is particularly important in the early stages of dyeing when the temperature is being raised and before the dyeing temperature has been reached. If dyeing times are to be minimized, it is clearly important that the dye goes onto the fiber uniformly in the first place and does not require lengthy leveling by desorption and resorption to produce a uniform product. In these ideal conditions it is not necessary to prolong the dyeing long beyond the time of maximum exhaustion to achieve the maximum penetration and color yield. However, it is clear that the times and temperatures must be dependent on the individual dyes present in the formulation and their concentrations.

Dyes

Some disperse dye manufacturers indicate in their shade cards the length of time necessary for individual dyes, at particular concentrations and under specified dyeing conditions, to reach effective equilibrium between the fiber and the bath, and also

maximum penetration and color yield. Although dyes with similar dyeing characteristics (high, medium or low energy) may be selected for a particular formulation, it is important to recognize that the actual dyeing rate of each component will be dependent on the concentration present in the formulation. The lower the concentration, the more rapidly it will dye relative to the other dyes in the bath. Care should be taken that the dyeing conditions allow the slowest dyeing component to reach effective equilibrium.

Individual disperse dyes do not generally interfere with one another when dyed as mixtures. Unlike acid dyes on nylon, disperse dyes do not block one another from dyeing efficiently. The phenomenon of blocking will be treated in the chapter on acid dyeing nylon.

A group of disperse dyes take advantage of the phenomena mentioned in the preceding two paragraphs and offers a number of disperse dyes, each of which is a mixture of several dyes of similar energy level and general hue. Dyeings with these mixtures, either singly or in combination, are rapid because each component of the formulation is present at a relatively low concentration. For example, if a red disperse dye product contains five red disperse components at equal concentration, then a 1% owg dyeing will be completed in the time it takes the slowest of the red components to dye to a 0.2% owg depth.

Oligomers/Trimers

Polyester fibers invariably contain small percentages (1-4%) of relatively intractable, oligometric material, mostly a cyclic trimer (three molecules joined end-to-end in a ring) of ethylene terephthalate. In powder form this trimer is white, has a melting point above that of dyebaths, ca. 320C (610F), and is just soluble enough for some of it to be extracted from the polyester during dyeing. It can often be seen as a white dusty surface on packages or inside the dyeing machine.

Because any of this material dissolved during dyeing can precipitate during cooling, it has been found desirable to minimize the problem by dropping dyebaths at temperatures above the boil into specially built expansion tanks. This method is not practicable in the case of piece goods in rope form where creases and crack marks might develop, but it is still desirable to lower the temperature and drop the bath as quickly as possible. Nonetheless, it is periodically necessary to wash out pressure dyeing vessels at high temperatures and with some added alkali to assist in hydrolyzing and solubilizing this oligomeric trimer. Suitable cleaning conditions might be ca. 130C (265F) and five grams per liter caustic soda (8).

Miscellaneous

Other materials which show up in polyes-

ter dyebaths can include lubricants to minimize crease and crack marks and carriers, notably for polyester/wool blends where the presence of the wool dictates that the temperature cannot be raised much above the atmospheric boil. The carrier can also prevent the wool being cross-stained by the disperse dye.

Stripping

Stripping can be accomplished by treating goods in a blank dyebath with the addition of a nonionic leveling agent at ca. 130C (265F). However, if chemical destruction of dye is necessary, one to two grams per liter sodium hydroxide plus a reducing agent or a mildly acidic treatment with zinc sulfoxalate-formaldehyde (a reducing agent) or sodium chlorite (an oxidant used in bleaching) can reduce the shade to almost a white ground.

Prolonged treatment of polyester goods in alkaline solutions will cause weight loss due to hydrolysis of polyester at the fiber surfaces. This technique has been used purposely to produce denier-reduced polyester. Typical of all stripping techniques, once the surface of the fiber has been eroded it is very difficult to rework the goods to give the originally anticipated appearance.

Review

Disperse dyes can be distinguished from one another chemically by their fastness properties and by their dyeing properties. The most useful if somewhat indeterminate categorization is into the groups of low, medium and high energy dyes, which roughly corresponds to grouping them by their molecular size (rmm), sublimation, heat resistance, rates of dyeing and tendency to level.

The effects of drawing, heatsetting and the tension and temperature of treatment on the dyeing properties have been discussed, along with the effects of changing the denier and the introduction of additional monomers.

The batch dyeing of polyester and the influence of the variables of time, temperature and dyebath additives (including the dyes) have been touched on, as have the parallel processes of reduction clearing and stripping. ∞

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The Knack of Problem Solving

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apocryphal, story of how the chemical structure of benzene came to the German chemist August Kekulé (1829-1896) during a dream (3).

"I was sitting writing at my textbook but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures of manifold conformation: long rows, sometimes more closely fitted together all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning, I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream, gentlemen, then perhaps we shall find the truth. . . ." (4)

Perhaps being a dreamer is the ultimate knack to problem solving.

Notes and References

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- (2) Partington, J. R., *A History of Chemistry*, MacMillan, London, 1962, Vol. II, pp782-798.
- (3) Though often repeated in the history of science, it is highly doubtful that Kekulé discovered the benzene structure in a dream. He first told the story 25 years after-the-fact at an affair in his honor, and more than likely, told it as a spoof of his colleagues. John H. Wotiz and Susanna Rudofsky, "Kekulé's Dreams: Fact or Fiction," *Chemistry in Britain*, Vol. 20, No. 8, August 1984, pp720-723.
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