Chapter 2: Direct Dyes and Their Application

By J. R. ASPLAND, School of Textiles, Clemson University, Clemson, S. C.

TO reiterate a definition from Chapter 1 (TCC, October, p14), direct dyes are "anionic dyes substantive to cellulose when applied from an aqueous bath containing electrolyte" (*1*).

During the 1980s, the more than 200 direct dyes listed in the AATCC Buyer's Guide (*2*) by their Colour Index Names— i.e., with chemically distinct structures— have been available in the U.S. as about 800 commercial products from the different direct dye suppliers. Of these products about 25% are blues, 20% each are reds and yellows, 10% are blacks with greens bringing up the rear at about 4%. This represents a complete range of hues, even though few of the dyes are noted for their brightness of shade.

Not all of these dyes have had their structures published, and therefore, many of them do not have the five-digit Colour Index Numbers which indicate where their structures can be found in the Colour Index (*3*).

Cellulosic fibers can be dyed with more different application categories of dyes than any other fiber type, being dyeable with direct, sulfur, vat and fiber reactive dyes as well as with azoic combinations. Of these application categories of dyes, direct dyes are second only to sulfur dyes in their textile usage worldwide, with vat and fiber reactive dyes well behind.

Since there are advantages and disadvantages associated with colors from all these application categories, it is imperative that those who select dyes for cellulosic fibers know as much as possible about the characteristics of all the contenders. Selection is made more difficult because of the wide range of application and performance characteristics within each application category, making it potentially dangerous to generalize about a group of dyes as a whole.

Direct Dye Classification

To assist in dye selection, most dye application categories can be subdivided in a number of ways. In the case of direct dyes, individual dyes can be classified by the chemical nature of their chromophores, which are the chemical groups primarily responsible for their color. They may also be classified by their dyeing characteristics. A third alternative is that they may be characterized by their fastness properties. As will be seen, the end-uses to which direct dyed fabrics might be put depend heavily on the fastness properties of the dyes used.

Of these three possible ways of classifying direct dyes, the first is of least importance to the dyer, although of considerable importance to those interested in dye chemistry. For example, it can be readily shown that direct dyes containing the azo chromophore (see later) can show widely different fastness and dyeing characteristics while still showing remarkably similar looking structures.

Lightfastness, or resistance of a dyeing towards fading on exposure to light, is often represented as a number on a scale of 1 to 8 (*4*). A rating of 1 is extremely poor, an 8 extremely good. For any dye, lightfastness ratings usually increase with increasing depth of shade. C.I. Direct Yellow 8 on cotton has a lightfastness rating of only 1-2 in heavy depths and a rating of 1 in light depths. By contrast, C.I. Direct Yellow 27 has a lightfastness rating of 5 in heavy depths and 4 in lighter depths. Yet the basic chromophore of these two dyes is essentially the same. Direct Yellow 27 contains only a sodium sulfonate group, $-SO_3Na$, and a methoxy group, $-OCH_3$, added onto the basic structure of Direct Yellow 8. The structures can be found in the Colour Index; their C.I. Numbers are 13950 and 13920, respectively. It is possible to list a number of equally demonstrative examples, but the point is made— structural classification is of limited value to the dyer or his customer. Instead we will move to how the Society of Dyers and Colourists classifies direct dyes by their dyeing characteristics (*1,5*).

Dyeing Characteristics

The SDC's classification of direct dyes is essentially based on the compatibility of different groups of direct dyes with one another under certain conditions of batch dyeing. That is to say, dyes which fall in any one of these SDC groups have dyeing characteristics similar to other dyes which fall in the same group, and characteristics different from those which fall in other groups. There are three groups: A, B and C.

● Class A: Self Leveling Direct Dyes. Dyes in this group have good leveling characteristics and are capable of dyeing uniformly even when the electrolyte is added at the beginning of the dyeing operation. They may require relatively large amounts of salt to exhaust well.

● Class B: Salt Controllable Dyes. These dyes have relatively poor leveling or migration characteristics. They can be batch dyed uniformly by controlled addition of electrolyte, usually after the dyebath has reached the dyeing temperature.

● Class C: Salt and Temperature Controllable Dyes. These dyes show relatively poor leveling or migration and their substantivity increases very rapidly with increasing temperature. Their rate of dyeing is controlled by controlling the rate of rise of the dyebath temperature as well as

ABSTRACT

Characteristics, classification, dyeing behavior and fastness properties of direct dyes are discussed. Factors which affect the results of direct dyeing include the use of dyebath additives and pH control, as well as dye selection and control of the liquor-to-goods ratio. Aftertreatment of direct dyeings to improve fastness properties is also discussed.

KEY TERMS

Aftertreatment
Batch Dyeing
Cationic Fixing
Continuous Dyeing
Diazotization/Coupling
Direct Dyes
Dyebath Additives
Dyeing Characteristics
Fastness Properties
Fiber Blends
pH Control
Preparation
Salt Rinsing

Direct Dyes

controlling the salt addition. Some of these dyes require very little salt to show good exhaustion in light shades.

While many Class A and Class B dyes can be dyed together, as can Class B with Class C dyes, it is undesirable to use Class A and Class C dyes together since their performance in the dyebath will be so very different.

Differences in behavior between the three dye classes will be illustrated later (Fig. 1), but first it might be desirable to define four dyeing terms which have already been introduced and which will be widely used in future chapters of this series. All are closely interrelated.

● Desorption. Desorption is the reverse of dyeing. Dyeing is the sorption of dye by the fiber; desorption is the loss of dye from the fiber and its transfer back into water.

● Stripping. The term stripping is used here in the same sense as is desorption. Stripping is the physical process during which dye moves from the fiber into the batch. It should not be confused with chemical stripping, which is the process whereby color is oxidatively or reductively destroyed, either on the fiber or in the bath, after the dye has first been physically desorbed (stripped) from the fiber.

● Leveling. Leveling is the process by which dye may be first stripped or desorbed from a dyed area of higher concentration on a fiber or fabric, followed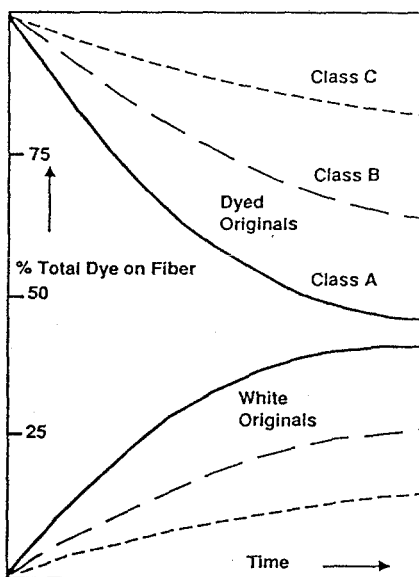 by its resorption or dyeing onto an area of lower concentration. The net result of leveling is to make the fiber content of a dyebath more uniform in shade overall. Leveling is a direct result of the intrinsic reversibility of the dyeing process, as discussed in Chapter 1.

● Migration. The term migration means movement from one place to another, with dye as with birds and animals. To this extent, desorption and stripping are both migration of dye from the fiber and into solution. Leveling is migration of dye from higher to lower concentrations on the fiber via the dyebath. A much more problematic manifestation of migration is the movement of dyes, along with the water, towards the evaporating surface during a drying process. (See the upcoming section on aftertreatment.)

Fig. 1 shows the general dyeing characteristics of Classes A, B and C direct dyes with respect to migration or leveling. It illustrates the behavior of the system when equal amounts of dyed and undyed cotton fabrics are entered into a dyebath containing a nominal concentration of salt and in nominal dyeing conditions; e.g., 10% sodium chloride on the weight of the goods, 90C (195F) and 30:1 liquor-to-goods ratio. If the concentrations of the dyes on the dyed fabric initially are called 100%, the figure shows how dye is lost from the dyed fabric and gained by the undyed fabric in increasing amounts as the time of dyeing progresses. This is both migration and leveling.

Class A dyes migrate substantially from the higher to the lower concentration on the fabrics and, if the time is sufficient, the dye becomes equally distributed between all the goods. Class B and C dyes migrate with increasing reluctance. It is important to realize that the rates of migration vary considerably from dye to dye and with different dyebath conditions but that the generalized relationship between Classes A, B and C holds.

Fastness Properties and End-Use

Direct dyes can be valuable for a wide variety of textile end-uses such as drapery and upholstery fabrics, lining and apparel fabrics and even some automotive fabrics. While it is fair to say that as a group direct dyes do not exhibit the highest standards of wetfastness, it is also fair to say that there are many applications for which individual dyes have very suitable fastness properties. It is the differences between the fastness properties of the individual direct dyes which makes dye selection a matter requiring great care.

All fastness tests on dyeings depend to some degree on the amount of dye on the fiber, with washfastness and wetfastness diminishing as the concentration of dye increases, whereas the reverse is true of lightfastness. In contrast to lightfastness, the other colorfastness properties, including washfastness, are measured on a scale of 1 to 5, where 1 is very poor and 5 is excellent. It is quite normal to evaluate fastness properties in half-steps such as, for example, 3-4.

From an examination of manufacturers' shade cards for about 70 direct dyes dyed on cotton, at concentrations of from 0.1 to 4.0% owg, the following fastness figures illustrate the diversity of properties delivered by the direct dyeings. *Note*: For details of the fastness testing methods, the current AATCC Technical Manual should always be consulted (6).

● II-A Washfastness: Average shade alteration of the original, 3; highest, 4-5; lowest 1. Average staining of adjacent cotton, 2-3; highest, 4; lowest, 1. The average values for washfastness can be increased by about half a grade by postfixation with a resin fixative and by about one grade by a durable press or crease resist resin finish.

● Lightfastness (Xenon Arc): At the heaviest depths recorded, the average lightfastness was 6, and ranged from 7 to 1. Not only does the lightfastness fall as the depth of shade is decreased, but if the fading light source is a carbon-arc there is usually a loss in lightfastness rating of about one grade.

Direct Dye Selection

Between consideration of the end-use fastness requirements for the goods to be dyed and dyeing compatibility characteristics of the dyes to be used, the number of suitable dye combinations for matching particular shades will already have been considerably reduced.

There are at least three more important questions that must be raised and answered before final selection of the most suitable direct dyes can be made:

● What particular method of dye application is to be used? The answer will depend on the nature of the dyeing equipment available and the physical form of the goods to be dyed. It could influence dye selection. Here we will consider mainly batch and continuous application methods in general. The use of individual types of dyeing equipment will be introduced only for purposes of illustration.

● What aftertreatments are appropriate? Such treatments can cause temporary or permanent changes in the structure and the fastness properties of the dyes and have different impacts on the dyeing economics and the complexity of the process.

● Are the goods being dyed 100% cellulosic or a blend? If the goods are a blend, how will dye selection affect the cross-staining of the other fibers present, which in turn will affect the shade and the overall fastness? How might the choice of dyeing procedures for the blend influence the suitability of particular direct dyes?

In practice, if you cannot answer these questions to your own satisfaction, you should consult your dye supplier.

Fig. 1. The migration or leveling of direct dyeings treated with undyed goods in a salt bath under nominal conditions.

Batch Dyeing

The variables which play a part in the uniform batch dyeing of direct dyes onto cellulosic fibers can be divided into two categories—those which are related to the molecular structure of individual dyes and those which are not.

The rates at which dyes go onto and come off the fibers are intrinsic to the particular dye structures, and account for the rates at which the dyebath is exhausted, the extent to which the dyebath is exhausted at equilibrium and the likelihood of dyeing uniformity. Another intrinsic property of direct dyes important in dyeing is their solubility in water.

But these intrinsic properties can all be controlled by such external or extrinsic factors as the preparation of the fabrics or fibers, the softness of the water, the time, temperature and rate of change of temperature of the dyeing, the electrolyte concentration used in the dyeing and when it is added, the liquor ratio and the rate of circulation of the liquor through the fibers, the pH of the bath and any other chemical additives or auxiliaries which might be used in the dyebath, including other dyes.

In other words, these variables, which taken together constitute a dyeing procedure, can affect the outcome of a batch dyeing, and they can be augmented by variables resulting from preparation and water quality.

It has long been recognized by statisticians that taking a complex system of variables and changing them one at a time is a very inefficient way to optimize a process. But with as many variables as batch dyeing has, it does no harm to have a qualitative idea of what might happen when particular process changes are made. For this reason, with apologies to the statisticians, we will examine one at a time some of the external factors which might control dyeing.

Preparation

Inadequate preparation probably accounts for more dyeing problems and defects than any other single cause. Unfortunately, there is no completely satisfactory method of assuring the uniformity of removal of adventitious soils, natural soils and fiber processing aids from textile goods that does not involve a multiplicity of samples and laborious comparative testing. The method of preparation that gives the most consistent results is usually the most rigorous one that can be afforded. However costly this may be, good preparation is like taking out an insurance policy against off-quality dyed goods and expensive reworks. Nonetheless, certain cellulosic goods can be scoured and even scoured and bleached at the same time as dyeing with direct dyes. The methods are usually reserved for jigs and becks and require alkalis, nonionic detergents and hydrogen peroxide or sodium perborate. The dyes
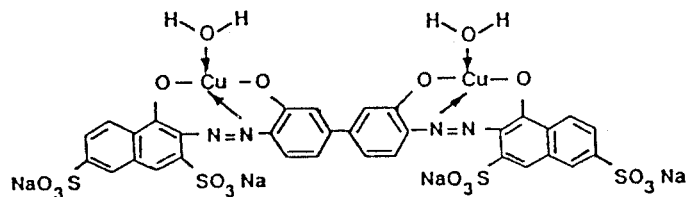

Fig. 2. C.I. Direct Blue 98.

must be selected to avoid those sensitive to alkalis and alkaline oxidation.

Water Quality

There are several metal ions which, in very small amounts, can cause shade change problems with direct dyes. They are calcium, magnesium, copper and iron, of which the first two can easily be present in cotton. The normal means of removing these metal ions involves the use of sequestrants such as EDTA or NTA (ethylenediaminetetraacetic acid or nitrilotriacetic acid) both of which are capable of removing some of the copper from premetallized direct dyes such as C.I. Direct Blue 98 (Fig. 2). Sodium hexametaphosphate is the preferred sequestrant for such dyes. When dyeing the very few direct dyes which must be aftertreated with copper, addition of a sequestrant is important to ensure that no stray metal ions complex with the dyes prior to the appropriate aftertreatment.

Small residual amounts of chlorine containing chemical species, used to purify water, can affect many dyes. This is particularly problematical if the amounts are as high as 1 part per million (ppm or mg/liter) and variable. In these circumstances, antichlors such as sodium bisulfite, $NaHSO_3$, or sodium thiosulfate, $Na_2S_2O_3$, should be added to all water in which dyes are to be dissolved.

Time

There are dyebath conditions which cause the gradual destruction of the dye. For example, alkali in the presence of viscose rayon can cause reduction of azo dyes, and the high temperatures associated with dyeing the polyester portion of polyester/cellulosic blends, such as 130C (265F), can cause dye hydrolysis. But in general, extending the time of dyeing usually results in increased dye uniformity.

Temperature

There are several diverse dyeing factors which are associated primarily with temperature. These include the rate constant of dyeing, k(dye), and the rate constant of stripping, k(strip), as defined in Chapter 1. At the end of the dyeing cycle these control the percentage dye exhaustion. But none of these factors can be completely dissociated from the other dyeing conditions such as liquor ratio and electrolyte concentration.

Temperature of Maximum Exhaustion

If electrolyte concentration and liquor ratios are held constant at a nominal level within the normal range, direct dyes can show the following behaviors: With exhaustion rising as the final dyeing temperature is increased to 100C (212F); e.g., C.I. Direct Blue 218. With maximum exhaustion at 20C (68F); e.g., C.I. Direct Yellow 12. With exhaustion which rises to a maximum and then falls with a further increase in the dyeing temperature; e.g., C.I. Direct Orange 72 and Red 81, with maximum exhaustion at 80C (176F) and 60C (140F), respectively.

It would make no sense to use dyes with maximum exhaustion temperatures of more than about 80C (176F) for jig dyeing if the temperature of the fabric roll does not exceed this temperature, as is indeed the case with many jig dyeing operations. If dyes of different temperatures of maximum exhaustion are mixed, there is no way to achieve a fully exhausted dyebath under normal dyeing conditions and there will be a good chance of lot to lot shade variation unless the dye cycle is very carefully controlled.

High Temperature Stability

Interest in high temperature dyeing of man-made fiber/cellulosic fiber blends, particularly polyester/cotton blends, either as yarn in package dyeing machines or as fabrics in beams and in jets, has made it necessary to be able to select direct dyes which are not susceptible to hydrolysis (chemical attack by water) at temperatures as high as 130C (265F).

There are many suitable dyes of high temperature stability—e.g., C.I. Direct Yellow 105, Orange 39 and Blue 80—but there are also some which are unsuitable; e.g., C.I. Direct Yellow 44, Red 80, Red 83.

Electrolyte

As seen in Chapter 1, the presence of sodium anions causes the chemical potential of direct dyes in solution to rise. As a result, the substantivity rises as does the percentage exhaustion at the end of the dye cycle, while the solubility falls.

The most common sources of sodium ion are sodium chloride, NaCl, (common salt); anhydrous sodium sulfate, Na_2SO_4; and Glauber's salt, sodium sulfate decahydrate, $Na_2SO_4 \times 10\ H_2O$. One gram of sodium chloride contains the same amount

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of sodium ion as 1.22 grams of sodium sulfate or 2.78 grams of Glauber's salt. It should be clear that the name Glauber's salt should not be used to include both anhydrous sodium sulfate and sodium sulfate decahydrate, for this could easily lead to serious errors in making up dyebaths.

Sodium sulfate and sodium chloride can be used interchangeably. But the more economical sodium chloride has a much higher tendency to corrode stainless steel under the high temperature conditions possible in package or jet dyeing machines. Sodium sulfate is preferred for these applications despite its slightly higher cost.

How much of the chosen salt should be added to a dyebath? The easy answer is enough to ensure good exhaustion but not enough to precipitate the dye. The amount will vary with the depth of shade being dyed, the weight of the goods and the liquor-to-goods ratio.

Traditionally, both the dye and the salt requirement of a dyeing have been expressed as percentages on the weight of the goods being dyed (% owg). But the amount of salt must be increased with increasing dye concentration (Fig. 4b, Chapter 1), and also increased with increasing liquor ratio (Eq. 7., Chapter 1) to ensure the same percentage exhaustion. If the amount of salt is pegged to both the percentage of dye being used and the amount of liquor, these problems will both be taken care of. This can be expressed in terms of a simple equation:

$$\text{Conc. of Salt (g/L)} = \% \text{ Dye owg} \times 10 \qquad \text{Eq. 1.}$$

For some cases, a factor other than 10 might be more appropriate, but this simple equation allows for a wide variation in both liquor-to-goods ratio and dye concentration to be handled easily. It would be most unusual for concentrations of salt to be less than 4 grams per liter or more than 40 grams per liter.

When must the salt be added? For dyeing equipment with very rapid circulation—e.g., with some jet and package dyeing machines—or when mixtures of Class A dyes are being used, then the electrolyte may be added at the beginning of the dyeing cycle. When Class B or Class C dyes are used, salt additions are best made after the dyeing temperature has been reached and sustained for about 10 minutes. The salt can then be added in from three to five portions. It is important that approximately 10 minutes be allowed between each addition, and that the additions start small and increase in size. This precaution is taken in order not to shock the system and cause the dye in the bath to exhaust suddenly, causing unlevelness. One of several possible salt addition schedules calls for 1/7 of the salt to be added, followed by 2/7 and finally the remaining 4/7, followed by a final 10 minutes at the dyeing temperature.

Dyebath Additives and pH Control

Direct dyes are normally applied at or around pH 7. The solubility of some direct dyes is increased at alkaline pH's and dyeing alkaline may slow the rate of exhaustion. There is a possibility that some ionization of the cellulose may occur to produce cellulosate ions. These bear a negative charge and may repel the dye anions. This phenomenon is studied more closely under the heading fiber reactive dyes.

On the other hand, for blended fibers, direct dyes may be in combination with other categories of dyes, such as disperse or acid dyes, where the preferred dyeing pH may run from 4 to 6. Some direct dyes seem to be sensitive in this pH range.

Dyeing viscose, particularly at elevated temperatures on the alkaline side, can lead to dye reduction and, since residual alkalis cannot always be removed from cellulosic fibers prior to dyeing, ammonium sulfate can be added to buffer the dyebath to a pH of slightly less than 7.

Apart from chelating agents and materials to adjust pH, a number of nonionic and anionic surfactants are sometimes added to the dyebath. Their precise functions are not always known but may be a combination of ensuring good penetration of the fibers by the dyebath, and providing the possibility for sequestering dye aggregates and dispersing any precipitated dye. Thus they might tend to lower the effective concentration of single dye molecules in the dyebath. The overall result can be a lower dyeing rate and improved dyeing uniformity. For this reason these dyebath additives may be referred to as dye leveling agents. A note of caution: It is easy to add chemical auxiliaries to dyebaths if they do not obviously interfere with normal processes of dyeing. It can be more difficult to demonstrate their utility. The cardinal rule to prevent addition of too many auxiliaries to dyebaths is: If in doubt, leave it out!

Liquor Ratio and Strike Rate

Dyeing processes operate at a wide range of liquor-to-goods ratios, ranging from approximately 30-40:1 for loose raw stock in open vessels and for garment dyeing; approximately 20-30:1 for becks; about 5-10:1 for jet dyeing machines; about 3-5:1 for package dyeing yarns and anywhere from about 0.6-2:1 for padding applications. As the liquor ratios get lower, the solubility of the dye and the effect of salt on that solubility gets more critical. The solubilities of commercial direct dyes can range from about 5-200 grams/liter at the boil.

Salt sensitivity is the property of dyes which indicates the extent to which the dyeing behavior, particularly the initial rate of dyeing, changes with the addition of salt. This initial rate of dyeing is frequently referred to as the strike rate. Dyes of high salt sensitivity, particularly at low liquor-to-goods ratios, can easily cause unlevel dyeings, because the strike rate is too high to allow for the dyeing uniformity which comes from good circulation between the dye liquor and the fibers.

In padding applications, differential strike rates in mixtures of dyes can lead to the initial preferential sorption of one or more of the components of the dye-mix by the fabric. The outcome would be a relatively higher concentration of the other dyes in the pad. This differential strike rate among the components of the dye-mix leads to another phenomenon known as tailing, in which the shade of the padded goods changes gradually along the length of the goods. Tailing may also be known as end-to-end shading. Dyes chosen for mixture shades should have as similar strike rates as possible. This is particularly important for continuous dyeing applications.

This will be covered in more detail in the upcoming chapter on sulfur dyes.

Continuous Dyeing

In the U.S. the nomenclature for batch dyeing and continuous dyeing is different. Batch dyers have always expressed the weight of dye to be used in terms of the percentage of dye on the weight of the goods and the weight of the dyebath in terms of the liquor-to-goods ratio. In continuous dyeing or padding operations, the term wet pickup has been substituted for liquor ratio. The wet pickup (wpu) of goods is the increase in the weight of goods after a padding operation compared with the initial weight of the goods before the padding operation, expressed as a percent. For example, if fabric weighing 100 grams before padding weighs 160 grams after padding, then the wet pickup of that 100 grams is 60 grams, and the percentage wet pickup is 60%. The dye concentration is usually given as the concentration of dye in the liquor through which the fabric passes in the padding operation. Between the concentration of dye in the pad liquor and the fabric wet pickup in padding, it is still hypothetically possible to calculate the percentage of dye on the weight of the goods, after padding:

$$\% \text{ dye owg} = [\% \text{ wpu} \times \text{dye in the pad (g/L)}]/1000 \qquad \text{Eq. 2.}$$

or

$$\% \text{ dye owg} = [\% \text{ wpu} \times \text{dye} \text{ in the pad (oz/gal)}]/133 \quad \text{Eq. 3.}$$

But in conditions of high strike rate, the results would be incorrect and misleading (see sulfur dyes in a later chapter).

The three principal processing sequences used for applying direct dyes in continuous or padding operations are: (i) pad-dry-chemical pad-steam; (ii) pad-steam; (iii) pad-chemical pad-steam. In process (i), the dye solution is in the first pad and the salt solution is in the second. In process (ii) both the dye and the salt are in the only pad, which makes it important to beware of salt-sensitive dyes. In process (iii) the first pad contains the dye and the second pad contains the salt. The wet pickup at the first pad is always much less than at the second, otherwise no salt would be picked up. This process resembles process (i) except that the cost of drying is saved.

In all these processes particular attention should be given to the choice of pad bath conditions so that tailing in dye mixtures is avoided. It requires the selection of dyes with similar strike rates under the given pad bath conditions. Tailing is further minimized by low volumes of pad liquor and a controlled rate of supply from the head tank to the pad liquor. In general, the best results are obtained with Class B dyes because Class A dyes tend to migrate during both drying and steaming while Class C dyes tend to strike too rapidly.

Some of the finer details of continuous dyeing will be considered in later chapters on vat and sulfur dyes because they are relatively more important than direct dyes in continuous dyeing.

Aftertreatment

Direct dyes are frequently aftertreated to overcome problems arising from their relatively poor wetfastness. The aftertreatments can range from a final rinse with a solution of electrolyte all the way to chemical reaction of the chromophore and formation of new dye structures. More than one aftertreatment can be used for any one dyeing.

Salt Rinsing

Rinsing, with up to 10 grams per liter of sodium chloride or sodium sulfate, will sometimes prevent migration of dye in the period between dyeing and drying when the goods might be lying around in a box. But this lay-time should be held to a minimum—certainly not more than five or six hours.

Treatment of the goods with magnesium salts has a similar but more marked effect, requiring a much lower concentration of the particular salt; e.g., 1 to 2 grams per liter. The bath must be free of dye before the treatment commences. Neither of these salt treatments improves the washfastness of the dyeing. They only diminish the tendency of the dye to migrate preferentially to the drying surfaces of the fabric.

Cationic Fixing

Cationic fixing agents are organic chemicals with large molecules which dissolve in water, dissociating into a large positively charged or cationic fragment, and a small negative ion such as a chloride ion. They may be resinous derivatives of cyanamide or quaternary ammonium compounds with long hydrocarbon chains.

The positive ion is attracted to the direct dye anion to form a large, complex salt molecule with very low solubility and, in consequence, much improved wetfastness. Once the number of cations has exceeded that of the dye anions, no more need be added. The amount depends on the depth of shade. Potential problems include shade changes and lowered lightfastness. Wetfastness can be markedly improved.

Copper Aftertreatment

The cupric copper cation, Cu^{2+}, could behave like the organic cationic fixatives, forming insoluble copper salts with the anionic dye molecules. Alternatively, it could form a co-ordination compound in which it is tied up into a more complex dye-metal compound such as those in premetallized dyes which generally have improved lightfastness as well as washfastness. A more detailed treatment of premetallized dyes will be given in the later section on acid dyes.

Copper salts are not environmentally desirable but the aftertreatments can be tailored to improve both wash- and lightfastness of some direct dyes without producing enough free copper ion in the effluent to cause problems.

This aftertreatment is no longer used except for a few economical heavy brown, navy and black shades. In these areas they collide head-on with sulfur dyes. More aspects of this topic will be covered later.

Diazotization and Coupling

Diazotization requires a free aromatic amine to be present in the dye, which can be treated with sodium nitrite and a strong acid followed by reaction with a compound containing an amino group, $-NH_2$, or a hydroxy group, $-OH$, attached to a benzene ring structure.

These reactions are called diazotization and coupling and produce a new azo group, $-N = N-$, with two nitrogen atoms sandwiched between two organic groups. This reaction will be discussed in some detail in a later section on azoic combinations. In the U.S. very few direct dyes are still treated this way. It is rather tedious but does improve the wetfastness, particularly of C.I. Direct Black 80 and Blues 2 and 120.

It has already been pointed out that durable press or crease resist resin finishing can raise the wetfastness of direct dyes, making then widely applicable in polyester/cotton blends. The effect is not permanent, and is eliminated if the resin is removed.

Dyeing Procedures And Fiber Blends

For most dyeing procedures involving only cellulosic fibers, there is little need to take the temperature of dyeing above an atmospheric boil (100C; 212F). As a result, direct dyeing procedures for cellulosic fibers are intrinsically rather simple. However, when cellulosic fibers are blended with other fibers—including wool, nylon, acrylic and, or course, the ubiquitous polyester—higher temperatures are sometimes required.

Because there are four more application categories of dyes which are suitable for application to cellulosic fibers, and because there are at least five other important fibers which might be blended with cellulosic fibers, it would seem much more appropriate to defer the treatment of blends until such time as all the categories of dyes for cellulose and other fibers have been treated. In that way, a comparison of the performance of all the possible dyes for cellulose can be made at the same time. For this reason this series will include a chapter on the dyeing of blends after all other individual dye application classes have been discussed.

Review

Direct dyes are widely used in dyeing cellulosic fibers partly because they require only the addition of simple salts for their application. They are water soluble, having a range of water solubility from about 5 to 200 grams per liter at the boil. They have a full range of hues but are not outstandingly bright. They can be classified in terms of their dyeing behavior or their fastness properties, and these fastness properties cover a very wide range. Nonetheless, for many of them, the washfastness leaves something to be desired. For this reason, there are a number of aftertreatments designed to improve this deficiency. The range and selection of these dyes is likely to continue to be large due to their economy and simplicity of application. ∞

References

(1) *Colour Index*, Society of Dyers and Colourists and AATCC, Vol. 2, Third Edition, 1971.

(2) *AATCC Buyer's Guide for the Textile Wet Processing Industry*, AATCC, published annually as the July issue of *Textile Chemist and Colorist*.

(3) Ref. 1, Vol. 4.

(4) *AATCC Technical Manual*, Vol. 66, 1991, p39.

(5) *The Dyeing of Cellulosic Fibres*, edited by Clifford Preston, Society of Dyers and Colourists, 1986, Chapter 5.

(6) *AATCC Technical Manual*, published annually.

A Series on Dyeing

A Series of Papers on Dyes and Their Application

By J. R. ASPLAND, School of Textiles, Clemson University, Clemson, S. C.

This series of papers, which will be published in *Textile Chemist and Colorist* over the next year or so, deals with the dyeing and coloration of normally fibrous polymeric materials in a manner which complements and extends the treatment of the subject given in the AATCC Dyeing Primer *(1)*.

The physical forms of materials made up of fibrous polymers can be very diverse, from raw stock through to knit or woven goods, and the variety of forms dictates the selection of machinery necessary for their handling. The fibers can be of at least eight widely different chemical types, with differing physical properties within each type, and as many as four or five types may be present in the same goods, although one or two is more usual. To accommodate the fiber variables, there are seven principal dye application categories. There are innumerable end uses for the goods, all requiring their own particular colorfastness properties. As a result, there are so many ways in which textile goods might be processed, and so many technical and aesthetic criteria possible for the end result, that most items of finished goods produced represent conscious compromises between the quality of the product and its cost of production.

Despite the magnitude of the subject, it does not require a strongly academic background to acquire a sound appreciation for the basics. There are general scientific principles involved which hold true throughout and these will be presented as and when the need arises. All the permutations and combinations of fibers, fabrics, chemicals, machinery, processes, end uses, commercial and other variables, can be followed if these basic principles are well understood.

This series is written primarily as an introductory text and source book for an American audience comprised of those in training for, or already working in, textile related areas, who wish to acquire a broad picture of the technology of dyeing and coloration or those who want to be guided to more detailed information on specific topics. Some of these readers may be textile undergraduates, with ready access to textile libraries; but the majority will undoubtedly be employed in the textile

organizations at locations where few technical reference works are available.

To simplify matters for the reader there will be a Bibliography, but few references in this text. Those references given will be written in English, published recently and relatively readily available.

The primary English language professional journals in the area are those of the American Association of Textile Chemists and Colorists (AATCC) and the Society of Dyers and Colourists (SDC) in the United Kingdom. The groups both publish and distribute a number of important reference works besides their journals. Most of the following Bibliography is taken from these reference works:

Bibliography

AATCC Publications

(1) Dyeing Primer, 1981.
(2) Buyers Guide, published annually.
(3) Analytical Methods for a Textile Laboratory, Ed. J. W. Weaver, 3rd. Edition 1984.
(4) Colour Index (published jointly with the SDC), Vols. 1-8 published and supplemented, 1971-1988.
(5) Technical Manual, annually.
(6) Book of Papers: International Technical Conference, published annually.
(7) Color Measurement Principles and the Textile Industry, 1990.

SDC and the Dyers' Company Publications Trust

(8) The Dyeing of Cellulosic Fibres, Ed. C. Preston, 1986.
(9) The Dyeing of Synthetic Polymer and Acetate Fibres, Ed. D. M. Nunn, 1979.
(10) Engineering in Textile Coloration, Ed. C. Duckworth, 1986.
(11) The Theory of Coloration of Textiles, 2nd edition, A. Johnson, 1989.
(12) Colour Physics for Industry, Ed. R. McDonald, 1987.

Other Reference Texts

(13) The Physical Chemistry of Dyeing, T. Vickerstaff, 2nd ed. Oliver and Boyd, London, 1954.
(14) Handbook of Chemical Specialties, John E. Nettles, Wiley and Sons, 1983.

General Organization

The series will be subdivided into four main sub-groups as follows:
- The Application of Anions to Nonionic Fibers
  (1) Cellulosic Fibers and Their Sorption of Anions
  (2) Direct Dyes and Their Application
  (3) Vat Dyes and Their Application
  (4) Sulfur Dyes and Their Application
  (5) Fiber Reactive Dyes and Their Application
  (6) Azoic Combinations and Their Application
- The Application of Ionic Dyes to Ionic Fibers
  (1) Nylon, Silk and Wool and Their Sorption of Anions
  (2) Acid and Mordant Dyes and Their Application
  (3) Acrylic and Modified Polyester and Their Sorption of Cations
  (4) Basic Dyes and Their Application
- The Application of Nonionic Dyes to Fibers
  (1) Nonionics and Their Sorption by Man-Made Fibers
  (2) Disperse Dyes and Their Application

About the Author

J. RICHARD ASPLAND has been professor of textile chemistry at Clemson University since 1982. Before that he was textile research manager for Reeves Brothers Inc. (1974-82), dye applications research group leader for the Sodyeco Division of Sandoz Chemicals Corp. (1966-74) and assistant professor in chemistry at the University of Manchester in Manchester, England. A native of England, he holds a BS in color chemistry and a master's in dyeing from Leeds University and a doctorate in textile chemistry from Manchester. A frequent contributor to TCC and a newly named member of its Editorial Board, he currently is on a year's sabbatical from Clemson to work on special projects for Ciba-Geigy AG in Basel, Switzerland.