CHAPTER 13

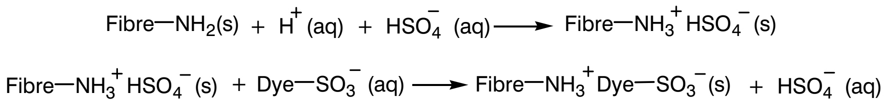
Acid, pre-metallised and mordant dyes

13.1 GENERAL DESCRIPTION OF ACID DYES

This chapter deals with acid, mordant and pre-metallised dyes. Despite their different names, these three types of dye have many features in common. They dye both protein and polyamide fibres using similar dyeing methods. In the Colour Index, they are classified as 'acid dyes' or 'mordant dyes'. The name 'acid dye' derives from the use of an acidic dyebath. Most pre-metallised and mordant dyes are acid dyes. In the case of mordant dyes, the dyeings are aftertreated with a suitable metal ion mordant, usually chromium. In fact, mordant dyes are often referred to as chrome dyes. The metal in pre-metallised dyes is incorporated into the dye molecule during the manufacturing process.

The dyeing properties of acid dyes vary widely (Section 13.2.2). The acids used in the dyebath range from sulphuric acid (dyebath $\text{pH} < 2.0$) to ammonium acetate (dyebath $\text{pH} > 6.5$). Acid dyes are usually sodium salts of sulphonic acids, or less frequently of carboxylic acids, and are therefore anionic in aqueous solution. They will dye fibres with cationic sites. These are usually substituted ammonium ion groups in fibres such as wool, silk and nylon. These fibres absorb acids. The acid protonates the fibre's amino groups, so they become cationic. Dyeing involves exchange of the anion associated with an ammonium ion in the fibre with a dye anion in the bath (Scheme 13.1).

Acid dyes have molecular weights in the range 300–1000 g mol^{-1}. The dyes with larger molecules have higher substantivity for wool or nylon. Such dyes have slower diffusion in the fibre and therefore less ability to migrate and dye level. The more hydrophobic, high molecular weight dyes therefore have better fastness to wet processes. Their absorption by wool and nylon also involves the interaction of



$$\text{Fibre—NH}_2\text{(s)} + \text{H}^+\text{(aq)} + \text{HSO}_4^-\text{(aq)} \longrightarrow \text{Fibre—NH}_3^+\,\text{HSO}_4^-\text{(s)}$$

$$\text{Fibre—NH}_3^+\,\text{HSO}_4^-\text{(s)} + \text{Dye—SO}_3^-\text{(aq)} \longrightarrow \text{Fibre—NH}_3^+\,\text{Dye—SO}_3^-\text{(s)} + \text{HSO}_4^-\text{(aq)}$$

Scheme 13.1

the dye with hydrophobic groups in the fibre. Dyeing is therefore not solely a consequence of simple ionic attraction.

The colour gamut of acid dyes is complete, including greens and blacks. The dyes are available as powders, grains and liquids for continuous dyeing, and as fine dispersions of the less soluble types. The selection of acid dyes for dyeing a particular material is not an easy matter, given the wide range of textile products and fastness properties demanded. Manufacturers recommend groups of selected acid dyes for each type of application. Compatible dyes are selected to have similar rates of dyebath exhaustion, when applied together by the recommended procedure, and similar fastness properties.

13.2 CLASSIFICATION OF ACID DYES

13.2.1 Classification according to chemical structure

Acid dyes are of many different chemical types. Sulphonated azo dyes constitute the major group and are mainly mono- and bis-azo compounds ranging in colour from yellow, through red to violet and brown. There are some navy blue bis-azo dyes that can build up to give blacks. The substantivity of azo dyes for polyamide and protein fibres is greater the higher their molecular weight and the lower the number of sulphonate groups per dye molecule. Many mordant and metal-complex dyes are also azo compounds. Their molecular structures are discussed later in this chapter (Sections 13.7.2 and 13.8).

Acid dyes usually have low substantivity for cellulosic fibres and do not give appreciable exhaustion onto them. Some of the higher molecular weight azo acid dyes, however, are difficult to distinguish from direct dyes for cotton (Chapter 14). The latter are often sulphonated bis-azo and polyazo dyes. There are therefore a number of acid and direct dyes with similar structural features that could be classified in either group. These dyes will dye wool, nylon and cotton. One feature that distinguishes acid dyes from direct cotton dyes, apart from their lower molecular weights, is that molecular planarity is not essential for acid dyes, but is for direct cotton dyes.

Anthraquinone acid dyes complement the azo dyes, ranging in colour from violet through blue to green. These dyes often have very good light fastness. Acid dyes with triphenylmethane (blues and greens) and xanthene (reds and violets) chromophores are less important types noted for their brilliant colours. These often have only poor light fastness. Sulphonated copper phthalocyanine dyes provide bright turquoise dyes of very good light fastness.

13.2.2 Classification according to dyeing characteristics

Acid dyes are commonly classified according to their dyeing behaviour, especially in relation to the dyeing pH, their migration ability during dyeing and their washing fastness. The molecular weight and the degree of sulphonation of the dye molecule determine these dyeing characteristics. The original classification of this type, based on their behaviour in wool dyeing, is as follows:

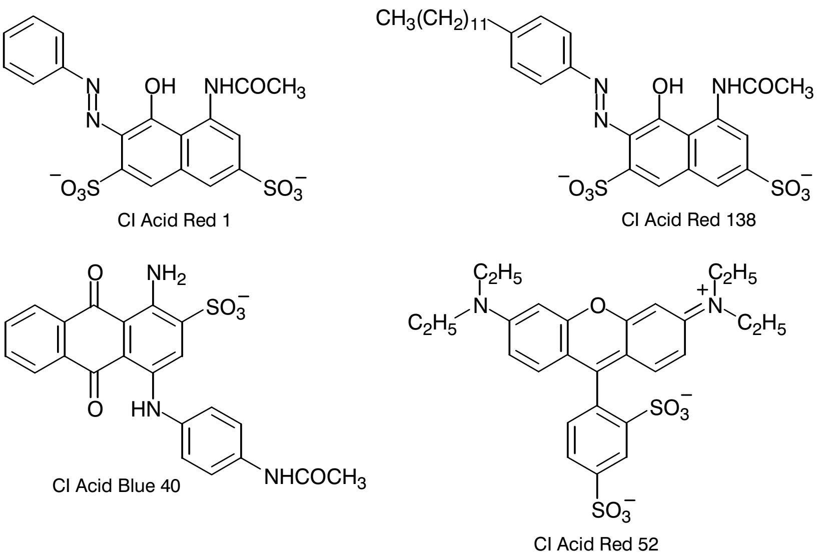
(1) level dyeing or equalising acid dyes;
(2) fast acid dyes;
(3) milling acid dyes;
(4) super-milling acid dyes.

Milling is the process in which a woollen material is treated, in weakly alkaline solution, with considerable mechanical action to promote felting. Dyes of good fastness to milling are essential to avoid colour bleeding during the process.

Table 13.1 Characteristics of the various types of acid dyes

	Levelling dyes	Fast acid dyes	Milling dyes	Super-milling dyes
Acid used	Sulphuric	Acetic	Acetic or NH_4^+	NH_4^+
Dyebath pH	2–4	4–6	5–7	6–7
Migration ability	High	Moderate	Low	Very low
Washing fastness	Poor–fair	Good	Very good	Very good
Molecular weight	Low	Moderate	High	Very high
Dye solubility	High	Moderate	Low	Low
State in solution	Molecular	Aggregated	Aggregated	Aggregated
Substantivity (pH 6)	Very low	Moderate	High	High

In the progression from levelling to super-milling dyes, the washing fastness improves gradually as the dye molecular weight increases and the number of sulphonate groups per dye molecule decreases. Larger molecules, with fewer sulphonate groups, have lower water solubility, migrate least during dyeing, and give dyeings of better washing fastness. They exhaust well on wool when dyeing in weakly acidic baths with a pH above 5. On the other hand, small dye molecules with many sulphonate groups migrate very well during dyeing and have poor wet fastness. For low molecular weight acid dyes the dyebath exhaustion is low when dyeing at a pH greater than 4. Acid dyes therefore show the usual inverse relationship of migration ability to wet fastness. Table 13.1 summarises the dyeing properties of the various types of acid dye. Note the difference in molecular structure between the levelling dye CI Acid Red 1 and the milling dye CI Acid Red 138 in Figure 13.1.


CI Acid Red 1

CI Acid Red 138

CI Acid Blue 40

CI Acid Red 52

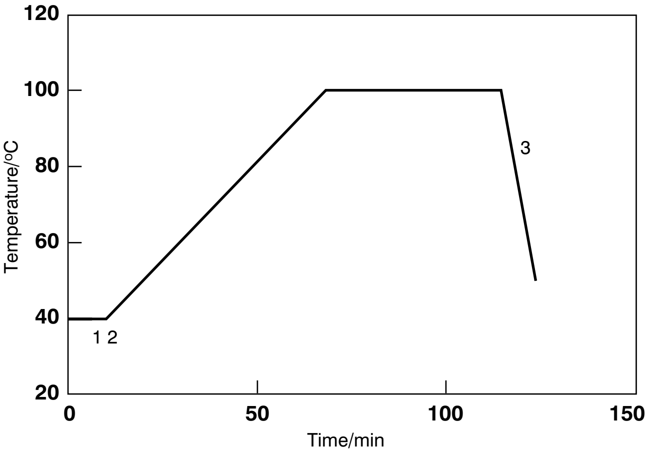
Figure 13.1 Chemical constitutions of some typical acid dyes

13.3 THE APPLICATION OF ACID DYES IN DYEING WOOL [1]

13.3.1 Levelling acid dyes

Dyeing wool with levelling acid dye requires sulphuric or formic acid in the dyebath, along with Glauber's salt, $Na_2SO_4.10H_2O$ (5–10% owf). Considerable amounts of a strong acid are needed to achieve good exhaustion, typically 2–4% owf of sulphuric acid. Under such acidic dyeing conditions, levelling acid dyes have rapid strike for the wool because of the high concentration of cationic ammonium ion groups in the wool. The dye molecules are not, however, firmly bound to these sites. Their good migration at the boil overcomes any initial colour unlevelness, provided sufficient time is allowed. If the initial dyeing is not quite on shade, the bath can be cooled somewhat, appropriate dyes added, and dyeing continued at the boil.

Because of the ease of migration of levelling acid dyes during dyeing, the fastness to washing of their dyeings is only from poor to moderate. Their light fastness, however, ranges from fair to good. These dyes are therefore used for pale to medium depths on wool fabric and yarn where a high degree of levelness is essential and good fastness to washing is not critical. In general, they produce much brighter shades than mordant or metal-complex dyes. Their relatively small molecular size provides high water solubility and good penetration into the individual fibres of tightly woven fabrics and high twist yarns. If the dye molecules do aggregate in solution at the maximum dyeing temperature, the aggregates are quite small, or there are enough individual molecules present in the solution for good penetration into the pores of the wool. Figure 13.2 illustrates a typical dyeing method.



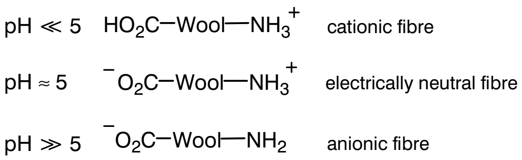
1 Add $Na_2SO_4 \cdot 10H_2O$ 5–10% owf
plus H_2SO_4 2–4% owf
2 Add dyes
3 Rinse

Figure 13.2 A typical dyeing procedure with level dyeing acid dyes

Wool contains about 820 mmol kg^{-1} of amino groups, some of which convert into ammonium ions in the presence of sulphuric acid, with a bound bisulphate anion. During dyeing, a dye anion displaces the bisulphate ion associated with an ammonium ion site (Scheme 13.1). In typical dyeings, only a very small fraction of the available cationic sites have associated dye anions. The wool is far from being saturated with dye anions. The displacement of simple anions in the wool by dye anions is a consequence of the dye's greater substantivity for the wool. Other possible types of dye–fibre interaction, besides ionic forces, will be discussed later (Section 13.4.2).

The added Glauber's salt acts as a retarding and levelling agent. Sulphate and bisulphate ions inhibit the initial rapid strike of the dye by occupying and thus blocking ammonium ion sites in the wool. Dye anions of higher substantivity then gradually displace the sulphate and bisulphate ions. These anions, however, do have slight substantivity for the wool and will displace some absorbed dye in acidic solution. The presence of Glauber's salt thus promotes levelling and reduces the dyebath exhaustion. Partial stripping of faulty dyeings is possible using 15–20% owf of Glauber's salt in an acidic bath at the boil. Level dyeing can also be controlled by using less sulphuric or formic acid in the initial bath. This gives fewer cationic sites in the wool. As dyeing proceeds, more acid is then gradually added to decrease the bath pH.

Levelling dyes give decreasing exhaustion on increasing the dyebath pH to values above 4, and with increasing temperature. These effects are consistent with a simple ion exchange process that is exothermic. Above the isoelectric point of wool around pH 5, the fibres become more anionic as the ammonium ions are then present in smaller numbers than carboxylate ion groups (Scheme 13.2). In weakly alkaline dyebaths, for example in the presence of dilute ammonia solution, levelling acid dyes readily desorb from wool fibres. This provides another method for stripping the colour from faulty dyeings.



Scheme 13.2

13.3.2 Fast acid dyes

These are usually monosulphonated acid dyes of somewhat higher molecular weight than typical levelling dyes. They dye wool by essentially the same dyeing method (Figure 13.2) using acetic acid (1–3% owf) and Glauber's salt (5–10% owf). They have reasonable migration at the boil. In some cases, a levelling agent may be recommended. These dyes are used where level dyeing is necessary but when the washing and perspiration fastness of levelling acid dyes are inadequate.

13.3.3 Milling acid dyes

These anionic dyes have higher molecular weights and greater substantivity for wool than levelling or fast acid dyes. They usually only have one sulphonate group per dye molecule and therefore have lower water solubility. They aggregate strongly, possibly even in boiling water, and give colloidal solutions. Dyeing with milling dyes is carried out in the pH range from 5 to 7, usually starting in the presence of sodium acetate or ammonium sulphate. Acetic acid may be added later in the process to promote exhaustion by increasing the number of ammonium ion groups in the wool. At best, milling dyes have low rates of diffusion in wool and poor levelling ability. Besides simple anion–cation attraction, other types of intermolecular forces bind the dye molecules to the wool. Milling acid dyes give dyeings with moderate to good washing fastness, better than for levelling acid dyes. In particular, they give dyeings that are reasonably fast to alkaline milling and with fair to good light fastness.

When dyeing with milling acid dyes, Glauber's salt is never added. Under typical dyeing conditions, at pH 6, it increases the exhaustion of such dyes and hinders levelling. The high concentration of sodium ions from the Glauber's salt helps to suppress the natural negative surface charge of the wool so that the dye anions are not repelled to the same extent and therefore have higher substantivity. The fibre's negative surface charge is much less evident in acidic solution when the wool has an excess of cationic ammonium ion groups. This effect of Glauber's salt is exactly the same as that of added salts in cotton dyeing and is discussed more fully in Section 14.4.1.

Because of the poor migration of milling acid dyes, level dyeing initially depends upon gradually increasing the dyeing temperature, and then possibly decreasing the dyebath pH by addition of a small amount of acetic acid. Some of these dyes have a tendency to stain cotton. They often have poor dyeing compatibility in mixtures and are preferred for self-shades (shades determined by the colour of a single dye).

13.3.4 Super-milling acid dyes

The super-milling acid dyes have much the same properties as milling dyes but are even more hydrophobic. They often have long alkyl chains in the dye molecule, give very good washing fastness, and good to very good light fastness. Super-milling acid dyes are widely used for yarn dyeing when the final fabric will be scoured and milled.

Dyeing wool with both types of milling dye in the presence of sulphuric acid at pH 3 results in very rapid absorption and unlevel dyeing, with no chance of levelling by migration. Dyeing is therefore started at about pH 6.5–7.0. The rate of dye absorption is controlled by the gradual temperature increase of the dyebath, and later by a gradual decrease in dyebath pH to complete exhaustion, if required. The initial pH of the dyebath must be even higher for dyeing pale shades to mitigate the initial strike. The pH can be lower for dyeing loose fibre and tops where levelness is less critical since the fibres will be blended together during spinning. Dyeing is slow below 60 °C. It may, however, increase rapidly above 70 °C, once the dye aggregates in solution begin to break up with increasing temperature. In the critical temperature range a decreased rate of temperature increase avoids uneven dyeing.

A typical wool dyeing procedure using super-milling dyes follows the scheme shown in Figure 13.2 except that the initial bath contains 2–3% owf of a weak acid such as ammonium acetate. The use of ammonium acetate or sulphate as the dyeing assistant gives a gradual decrease in the pH value as dyeing proceeds. It has been proposed that heating such ammonium salts in solution liberates ammonia, which escapes from the dyebath, thus giving a decrease in pH (Scheme 13.3). In fact, the pH of ammonium acetate or sulphate solution decreases slightly as the temperature rises even without ammonia loss. In some cases, ammonium phosphate provides some neutralising and buffering action if there is any residual alkali in the wool from scouring.

$$CH_3CO_2^- + NH_4^+ \longrightarrow CH_3CO_2H + NH_3$$

Scheme 13.3

Many milling and super-milling acid dyes give ‘skittery’ dyeings on wool despite using a gradual temperature increase to control the dyeing rate and the colour uniformity. Dyes penetrate more readily into the wool fibre in regions where weathering of the fibre tips or mechanical stress during processing has damaged the epicuticle (Section 7.2.2). If the dye is unable to migrate, the result is an uneven skittery dyeing. Skitteriness is the perceived uneven colour effect from pale and dark fibres in proximity. Goodall's dyeing method overcomes this. Dyeing is commenced at the boil, at relatively high pH in the presence of ammonia and its acetate. Under these conditions, the dye molecules readily penetrate into the swollen wool fibres. The pH gradually falls during dyeing as ammonia escapes and the dyeing rate slowly increases giving more uniform dyeings. Alternatively, proprietary levelling agents may be used (Section 13.5.3).

Colour stripping is difficult with higher molecular weight dyes of greater substantivity. Hot ammonia solution will remove some dye. This simply decreases the number of ammonium ion groups in the fibre so that anionic dye molecules held by ionic attraction are released. This may be assisted by a cationic/non-ionic auxiliary product that holds the anionic dye in the bath by complex formation and prevents its re-absorption by the fibres (Section 13.5.3). The non-ionic component keeps the dye–auxiliary complex in suspension and avoids its precipitation. Complete stripping of azo dyes is possible with reducing agents such as zinc sulphoxylate-formaldehyde, which split azo dyes into amines, thus destroying the chromophore. The stripping conditions should be as mild as possible because of the tendency of wool to felt. Long, vigorous stripping increases the risk of fibre damage and the development of a harsh handle, especially under alkaline conditions.

Under neutral conditions, wool is slightly anionic, with more carboxylate than ammonium ion groups. Even so, super-milling dyes exhibit high substantivity. The desorption of super-milling dyes from dyed wool is only slight in solutions with a pH value of up to 9.5. This shows that the dye binds to the fibre by forces other than the electrostatic attraction between ions of opposite charge. Desorption only becomes significant above pH 9.5 as the wool fibres begin to swell more. A dyeing mechanism based on simple ion exchange does not explain the high fastness to washing of these dyes. Other intermolecular forces are obviously involved, including dipole, dispersion and hydrophobic interactions (Section 13.4.2).

13.4 MECHANISM OF WOOL DYEING [2]

13.4.1 Absorption of acids by wool

Wool contains about 820 mmol kg^{-1} of amino groups. Under acidic conditions, some of these will accept protons to form ammonium ions. These cationic groups are capable of binding dye anions by ionic attraction. Practical dyeing with acid dyes, even in the presence of sulphuric acid, only involves a very small fraction of the available cationic sites. Saturation of all such potential sites in acidic wool with a simple acid dye such as Orange II (Figure 1.1, molecular weight 350 g mol^{-1}) corresponds to almost a 30% owf dyeing.

Figure 13.3 shows the molar amount of acid combined with wool at equilibrium as a function of the pH of the solution, as well as some similar data for dyes in the form of their free sulphonic acids. Each dye has a limiting pH above which the dye does not absorb. This pH is higher the greater the substantivity of the dye. Thus, the curves in Figure 13.3 shift to higher pH as the dye substantivity increases because of dye–fibre interactions other than those involved in ion exchange.

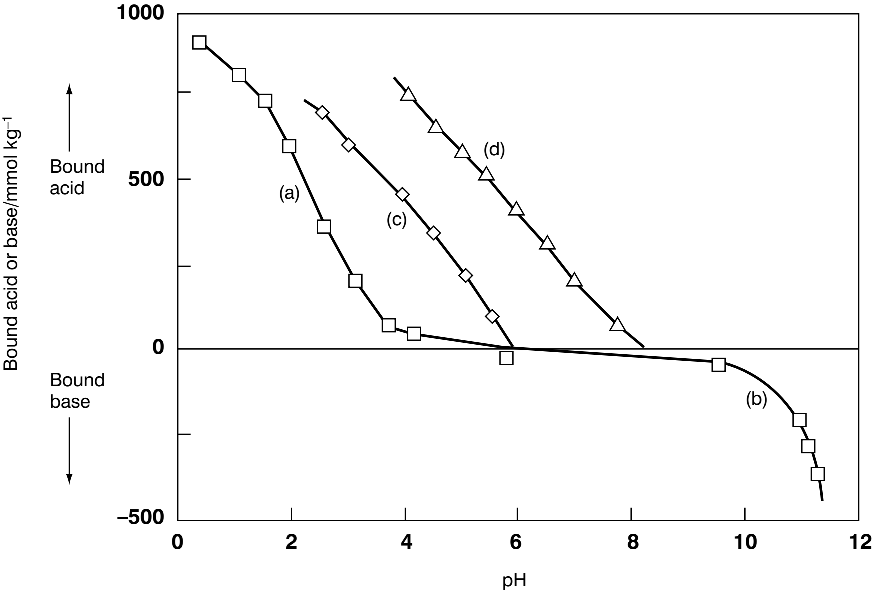


Figure 13.3 Amounts of combined acids and bases for wool. Absorption of HCl (a), NaOH (b), a simple levelling acid dye (c) and a high substantivity acid dye (d)

In wool, the numbers of amino and carboxylic acid groups are almost equal (820 and 770 mmol kg^{-1}, respectively). Because these belong to different amino acid units, wool only absorbs small amounts of acid or alkali in the pH range from about 4 to 9 (Figure 13.3). The isoelectric point, where the wool contains equal numbers of cationic and anionic groups, occurs at about pH 5–6.

13.4.2 Ion exchange and hydrophobic bonding

Wool strongly absorbs milling and super-milling dyes even under weakly alkaline conditions when the fibre has more anionic carboxylate groups than ammonium ion groups. These dyes give high dyebath exhaustion under these conditions. The ion exchange mechanism is clearly an oversimplification and other modes of dye–fibre interaction must operate in these cases.

The substantivity of acid dyes for wool generally increases with increase in the dye molecule surface area but decreases when the dye has additional sulphonate groups in the molecule. For large hydrophobic dye molecules, other types of dye–fibre interactions become important besides the coulombic attraction between ammonium ion groups in the wool and dye anions. These additional dye–fibre forces may involve dipole interactions, hydrogen bonding, and dispersion forces operating between groups in the dye molecule and appropriate groups in the protein. Wool, silk and nylon all have regions along the polymer chains that are quite hydrophobic, being void of ionic and polar groups. Dye–dye and dye–fibre hydrophobic interactions might be expected in such regions.

Hydrophobic bonding is simply the term used to describe the tendency of hydrophobic groups to associate together to avoid interaction with water, as in the formation of soap micelles and dye aggregates. The driving force in hydrophobic bonding is the collapse of the hydrocarbon–water interface that occurs when the hydrophobic groups in the dye molecule interact with hydrophobic groups in the wool. Water molecules tend to become more highly hydrogen bonded together, and therefore more highly structured, at an interface with a hydrophobic group. When the hydrophobic group is surrounded by other hydrophobic groups rather than water, the water molecules liberated give a significant increase in entropy. This explanation of the substantivity of the more hydrophobic acid dyes has considerable merit.

Evidence for the importance of hydrophobic interactions comes from dyeing experiments on chemically modified wool. Wool in which all the free amino groups have been benzoylated by treatment with benzoic anhydride, shows enhanced absorption of typical milling dyes, but reduced absorption of low molecular weight levelling acid dyes that have several sulphonate groups per dye molecule. In wool dyeing, dye–fibre interactions therefore range from purely ionic interactions between dye anions and ammonium ion sites in the wool to purely hydrophobic interactions between non-polar groups in the fibre and in the dye molecule. The consensus seems to be that the *extent* of absorption of acid dyes depends on the hydrophobic interactions between the dye and the wool, which also determine the washing fastness. The coulombic attractions between wool ammonium ions and dye anions, however, determine the *rate* of dyeing.

13.4.3 Kinetics of wool dyeing

Above about 40 °C, increasing temperature increases the dyeing rate with acid dyes but decreases the overall degree of exhaustion, in agreement with Le Chatelier's principle for an exothermic dyeing process. The rate of dyeing increases by decreasing the dyebath pH, even though the diffusion coefficients for acid dyes in wool are independent of pH. A lower pH increases the dye concentration on the available wool fibre surfaces by increasing the number of ammonium ion sites. This increases the concentration gradient for diffusion of the dye into the fibres. Diffusion into the fibre is usually considered to control the rate of dyeing. Because of this, wool fibres may be ring dyed at low dyeing temperatures. This implies rapid mass transfer of dye to the fibre surface and rapid adsorption, but slow diffusion into the fibre. At higher temperatures, when diffusion is faster, rate-controlling mass transfer of dye to the fibre surfaces can occur at low dye concentrations and when the relative movement of the goods and dye liquor is inadequate.

The kinetics of wool dyeing is quite complex. The penetration of dye molecules into wool fibres was discussed in Section 7.2.2. What is important from the practical viewpoint is to control the dyeing rate so that dye is absorbed neither too rapidly in the early stages of dyeing, giving unlevel coloration, nor so slowly that the process is uneconomic. The objective is to produce a level, well-penetrated dyeing in as short a time as possible. Some of the means of achieving this are discussed in the following section.

13.5 PROBLEMS OF DYEING WOOL LEVEL

13.5.1 Temperature and pH control

One of the major objectives of dyeing is to produce goods with an even colour. This is usually more of a problem when using rapid dyeing dyes that have little migrating capability. Unlevelness of a dyeing arises from:

(1) unequal access of the fibres to the dye solution, resulting from densely packed fibres or yarns and from poor agitation of the dyebath;
(2) variation of the temperature throughout the dyebath and the goods;
(3) uneven pH in the bath and the material.

Wool dyeing starts under conditions of low substantivity, at low temperatures and at higher pH. After alkaline scouring of undyed wool, the goods should be run in the dyeing machine in the presence of a buffer or weak acid to ensure complete and uniform neutralisation of any residual alkali in the wool. A high initial pH minimises the number of excess ammonium ion groups in the wool and avoids rapid initial dye adsorption. The rate of dyeing is controlled by slowly increasing the temperature of the bath, and possibly also by gradually decreasing the bath pH using additions of a weak acid, or by using a substance that releases a weak acid on hydrolysis, such as chloral hydrate or ethyl lactate (Scheme 13.4).

$$Cl_3C{-}CH(OH)_2 \longrightarrow CHCl_3 + HCO_2H$$

$$CH_3CH(OH)CO_2C_2H_5 + H_2O \longrightarrow CH_3CH(OH)CO_2H + C_2H_5OH$$

Scheme 13.4

Milling and super-milling dyes give a substantial increase in the dyeing rate at a critical temperature around 70 °C. This is probably because these dyes begin to de-aggregate extensively above this temperature. If temperature and pH control do not give adequate levelness, then proprietary levelling agents may be used. These are discussed in Section 13.5.3.

13.5.2 Dyeing damaged wool fibres

Both the thin epicuticle and the scales covering a wool fibre offer considerable resistance to dye penetration. Damage to these surface layers enhances the local dyeing rate compared to that of undamaged fibres. The damage may be of natural origin or a result of the severity of chemical processes during manufacture. Wool is a sensitive natural fibre. Fibres from different locations on a sheep have different dyeing properties because of differences in fineness (fine fibres dye more rapidly than course ones) and different degrees of weathering and abrasion. A wool fabric may also contain fibres damaged during setting, crabbing, decatising, scouring (alkaline), bleaching with hydrogen peroxide (alkaline), chlorination or carbonisation (acidic). Uniform treatment in these processes is essential. The kinetics of wool dyeing therefore depends upon the extent of fibre damage and the levelness of dyeing upon the uniformity of the distribution of damaged fibres.

Damaged wool fibres give two main types of unlevel dyeing:

(1) dyeings with coloured patches of different depths caused largely by uneven treatment with chemicals during processes such as scouring, bleaching or chlorination, or incomplete and non-uniform removal of the residual chemicals;

(2) skitteriness – the uneven dyeing of individual wool fibres whose tips have degraded more from the greater exposure to the elements during the growth of the wool fleece.

Wool fibres with damaged scales absorb dye more rapidly than undamaged fibres. Weathered tips of wool fibres tend to give skittery or so-called 'tippy' dyeings. The fibre tips may have surface damage and have undergone chemical modifications. They may dye lighter or darker in depth. In the more usual case, the damaged tips absorb more dye than the rest of the fibre and are darker. If the underlying protein is chemically changed because of weathering, lighter dyed tips sometimes arise because of their lower dye absorption at equilibrium compared to the undamaged fibre root. When dyeing with mixtures of dyes containing different numbers of sulphonate groups per dye molecule, the wool fibre tip may even dye a different shade than the root.

Skitteriness is much easier to see in dyed loose fibre. The colour of skittery dyeings is often weak. This is because a mixture of undyed and dyed fibres always gives a paler shade than the same total mass of evenly dyed fibre containing the same amount of dye. The colour strength of a skittery dyeing therefore improves if the dyes can migrate and the colour becomes more level. When dyeing with non-migrating dyes, the use of specific cationic or amphoteric auxiliary levelling agents avoids 'tippy' dyeings (Section 13.5.3).

Wool is a sensitive protein. Even dyeing with acid dyes at the boil causes some degradation, particularly on prolonged boiling to promote dye migration. This causes hydrolysis of various wool proteins. This is slowest around the isoelectric point at about pH 5. It is particularly rapid with alkaline solutions. Hydrolysis impairs the mechanical properties of the wool, giving more brittle fibres with decreased resistance to abrasion. If the goods are in the form of loose fibre, fibre brittleness can complicate carding and spinning. Hydrolytic damage of wool fibres also produces unacceptable yellowing. Certain protective auxiliary products are used to minimise degradation and yellowing of the wool. These protective agents are most useful for high temperature dyeing processes, such as the dyeing of wool/polyester blends at 120 °C, or when dyeing has to be extended or repeated. In wool dyeing, the conditions should always be as mild as possible, at as low a temperature as possible, and in weakly acidic solution.

Chlorination is one process deliberately used to modify the scale structure of wool fibres to prevent felting and shrinkage of woollen goods on washing (Section 7.4.2). The dyeing of chlorinated wool poses several problems. Acid dyes have increased initial substantivity for chlorinated wool because of the severely damaged scales. The rapidity of the reaction of chlorine with wool increases the risk of uneven chlorination resulting in subsequent unlevel dyeings, even when using levelling acid dyes. The dyeings also have lower washing fastness because of the increased ease of desorption of dyes from chlorinated wool. The difference in the dyeing behaviour of untreated and chlorinated wool appears to be entirely a consequence of dyeing rates since the two fibres give the same equilibrium dye absorption.

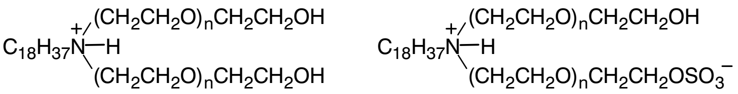
13.5.3 Use of wool dyeing assistants [3]

A wide variety of auxiliary products are used in wool dyeing to promote dye levelling. Levelling agents function by retarding dye absorption. They are of two main types: anionic and cationic/non-ionic. Wool adsorbs anionic levelling agents and they retard dye absorption by initially blocking the cationic ammonium ion sites. The more substantive dye anions eventually displace the anionic product. Anionic surfactants with long alkyl chains have higher fibre substantivity and are more effective, but they decrease the equilibrium uptake of the dye. Although the ion exchange explanation may be an oversimplification of the action of anionic levelling agents in wool dyeing, it adequately explains their retarding effect. Typical products are the sulphate esters of fatty alcohols, $R–OSO_3Na$.

The action of cationic/non-ionic levelling agents is quite different. Cationic agents form a complex with the anionic dye in the dyebath and prevent its uptake by the wool. The non-ionic portion of this type of product keeps the auxiliary–dye complex ($Dye^- Aux^+$) dispersed in solution. This is important to avoid its precipitation in the bath or on the material surface. Free dye molecules are liberated as the dyeing temperature increases since the complex is less stable at higher temperatures (Scheme 13.5). Strong levelling action can be achieved using a cationic polyethoxylated amine (such as **1**, Figure 13.4) with a short chain ($n = 5–20$), mixed with a purely non-ionic product to keep the complex in dispersion. The greater cationic character of products with short polyethoxylated chains gives strong complex formation, pronounced retardation of dyeing and a higher risk of

$$\mathrm{Dye^- + Aux^+ \longrightarrow Dye^-\,Aux^+}$$

Scheme 13.5

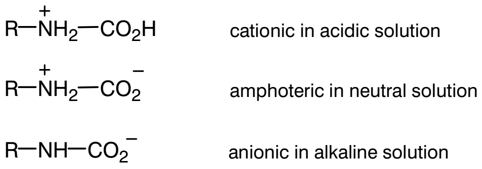


1 2

Figure 13.4 Cationic (**1**) and amphoteric (**2**) levelling agents

precipitation. When the polyethoxylated chain is longer (n > 50), the dye–auxiliary complex is dispersed by the cationic auxiliary product alone.

Some levelling agents are amphoteric, with both anionic and cationic groups present in the molecule. Their form in the dyebath depends upon the pH (Scheme 13.6). Amphoteric auxiliaries (such as **2,** Figure 13.4) help to eliminate differences in dye uptake between the roots and tips of wool fibres by increasing the rate of dyeing of the undamaged portions. The cationic portion complexes the dye in solution, the non-ionic chain ensures dispersion and solubility, while the terminal anionic group promotes substantivity for the wool surface. This is assisted by the dye–auxiliary complex being more hydrophobic than the uncomplexed dye. On chlorinated wool with a Hercosett polymer, however, the wool surface is more hydrophilic and such amphoteric products may have no effect or even retard dye absorption. Clearly, the choice of auxiliary products in wool dyeing requires care and experience.



$\mathrm{R{-}\overset{+}{N}H_2{-}CO_2H}$ cationic in acidic solution

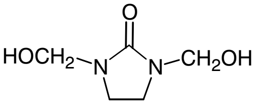
$\mathrm{R{-}\overset{+}{N}H_2{-}CO_2^-}$ amphoteric in neutral solution

$\mathrm{R{-}NH{-}CO_2^-}$ anionic in alkaline solution

Scheme 13.6

13.6 SPECIAL WOOL DYEING PROCESSES

High temperature wool dyeing, under pressure, decreases the dyeing time and is useful if additions are not required. At dyeing temperatures above 100 °C, the rate of levelling is higher but there is a risk of dye hydrolysis and chemical reduction of azo dyes by wool degradation products. Addition of a small amount of a mild oxidising agent prevents such reduction. Dyeing at 110 °C, for not longer than 60 min, at a pH around 5, avoids damaging the wool fibres. Dyeing at 120 °C is possible for wool/polyester blends but the dyebath must contain fibre-protective agents. These are often products that slowly release formaldehyde, such as dimethylolethylene urea (**3**, Figure 13.5), that are much safer and easier to use than free formaldehyde. The released formaldehyde probably provides some fibre protection by crosslinking ruptured cystine links. Other types of protective agents form a hydrophobic coating on the fibre surface.



3

Figure 13.5 Dimethylolethylene urea, a fibre-protective agent

Low temperature dyeing methods greatly reduce wool damage. These methods involve pretreatments to modify the wool, the use of solvents to modify the non-keratinous regions, or the addition of surfactants. Auxiliary chemicals are needed to assist dye penetration, otherwise ring dyeings result with inferior rubbing fastness. Dyeing in the presence of benzyl alcohol in an aqueous dyebath greatly increases the rate of dyeing and dyeing at temperatures around 80 °C is possible, thus minimising any degradation of the wool surface. Benzyl alcohol breaks up dye aggregates in solution and forms a layer of solvent at the fibre surface in which acid dyes are very soluble. The concentrated layer of dye solution at the fibre surface promotes more rapid diffusion. Dyebath exhaustion is complete and the bath containing the benzyl alcohol can be re-used. The Irga-solvent process (Ciba) is one such solvent-assisted method. Most current low temperature methods depend upon the use of special auxiliary products such as polyethoxylated alcohols with short chains, in combination with non-ionic dispersants with longer chains. These allow dyeing at 80–85 °C, with minimal fibre damage, and probably function much like benzyl alcohol.

There are also a number of processes for the continuous dyeing of loose wool and sliver that involve padding or spraying, followed by fixation in steam or by radio frequency radiation. The dye solution contains a thickening agent to prevent drainage through the fibre mass and a variety of auxiliary products.

13.7 MORDANT DYES FOR WOOL

13.7.1 Introduction

In Chapter 1, we saw how metallic mordants improve the fixation and fastness properties of dyes lacking substantivity for natural fibres. Many of the natural dyes were polygenetic. They gave different colours with different metallic mordants such as salts of aluminium, tin, iron or copper. Today, almost all wool mordant dyes have a chromic ion mordant (Cr^{3+}) and are therefore often called chrome dyes. The chromic ion is invariably complexed with the dye after the initial dyeing with an acid dye, to produce dark, dull shades of excellent light and wet fastness. The final hue is usually quite different from that of the original non-metallised dye so that colour matching is more difficult than in direct dyeing. The presence of chromium in the dyehouse effluent poses a severe environmental problem, because of its toxicity, particularly in the form of dichromate ion ($Cr_2O_7^{2-}$). Improved mordanting processes must minimise loss of this metal in the dyehouse effluent.

13.7.2 Basic principles of metal-complex formation

Transition metal ions in aqueous solution can interact with anions to form simple salts such as $FeCl_3$, which results from a combination of one Fe^{3+} and three Cl^- ions. They also combine with anions and neutral electron donors to form complexes involving coordinate covalent bonds. For example, potassium ferricyanide, $K_3Fe(CN)_6$, consists of three K^+ ions and one complex ion $Fe(CN)_6^{3-}$ (Scheme 13.7). Coordinate bonds involve sharing of electron pairs that originate with the anion or electron donor (Lewis base). The species providing the electron pair is a ligand. The orbital containing the lone electron pair of the ligand donor overlaps with a vacant orbital of the transition metal ion acceptor (Lewis acid). For a transition metal, the lowest energy vacant orbitals available are d orbitals or their hybrids. The maximum number of ligands that can attach to the metal ion is the coordination number. The most common values of this are 4 and 6.

In aqueous solution, four water molecules acting as ligands surround and hydrate the cupric ion (Cu^{2+}, coordination number = 4). Stronger ligands (stronger electron donors) such as ammonia can displace the water molecules to

$$Fe^{3+} + 6CN^{-} \longrightarrow Fe(CN)_6^{3-} \qquad \text{(Fe coordination number = 6)}$$

Scheme 13.7

form other complex ions (Scheme 13.8). If anions act as ligands, then the charge on the complex ion will be less than that on the hydrated metal ion and can be negative, as in the case of ferricyanide (Scheme 13.7), or even zero.

$$Cu(H_2O)_4^{2+} + 4NH_3 \longrightarrow Cu(NH_3)_4^{2+} + 4H_2O$$

Scheme 13.8

The bond between a ligand and the metal ion is a covalent bond and can be difficult to break if the ligand is a strong electron donor. For example, in a solution of the green complex salt $CoCl_3.4NH_3$, only one third of the total available chlorine precipitates as silver chloride after addition of silver nitrate solution. Two of the chloride ions act as ligands bonded to the cobalt ion to give the stable complex ion $Co(NH_3)_4Cl_2^+$. In this ion, the cobalt has a coordination number of 6 and the initial charge of the Co^{3+} ion falls to +1 because of the two chloride ion ligands bonded to it. The third chloride ion is the counter-ion to the complex cation and it is this that precipitates as silver chloride (Scheme 13.9)

$$Co^{3+} + 4NH_3 + 3Cl^- \longrightarrow Co(NH_3)_4Cl_2^+ + Cl^- \quad \text{(Co coordination number = 6)}$$

Scheme 13.9

The formation of complex ions involves overlap of vacant orbitals of the acceptor metal ion with the orbitals containing lone pairs of electrons from the ligand donors. In Pauling's valence-bond treatment, the type of vacant hybrid orbitals of the metal ion determines the coordination number and the stereochemistry. For example, chromium (electronic configuration $[Ar]4s^13d^54p^0$) forms the chromic ion (Cr^{3+}, electronic configuration $[Ar]4s^03d^34p^0$). The hybridisation of the empty 4s, two empty 3d and three empty 4p orbitals gives six vacant d^2sp^3 hybrid orbitals, each capable of accepting a lone pair of electrons from a ligand. On combination with six electron pairs from six ligands, all the orbitals are filled. They form an octahedral arrangement in the complex ion to minimise repulsions between the six bonds ($Cr(NH_3)_6^{3+}$).

Copper (electronic configuration $[Ar]4s^23d^94p^0$), on the other hand, forms cupric ion (Cu^{2+}, electronic configuration $[Ar]4s^03d^94p^0$), which promotes one electron from a 3d to a vacant 4p orbital to give the electronic configuration [Ar]$4s^0 3d^8 4p^1$. This permits formation of four vacant dsp^2 hybrid orbitals from the vacant 3d, 4s and 4p orbitals, which results in a square-planar arrangement of four ligand donors.

There are a number of aspects of coordination chemistry that Pauling's theory fails to explain and the newer ligand field theory has been more successful. For our purposes, it suffices to recall that chromium has a coordination number of 6 and that the ligands in a chromium complex give an octahedral arrangement around the central chromium atom. Copper usually has a coordination number of 4 and the four ligands form a square around the central copper atom.

Many ligands have more than one electron donor site and are bi-, tri-, or even polydentate (Figure 13.6). For example, ethylene diamine (1,2-diaminoethane) has two amino groups and is bidentate, whereas EDTA (Figure 8.1) is hexadentate (*hexa* = six, Greek; *dens*, *dent* = tooth, Latin). Note the relation to the French word *mordre* (to bite), the origin of the word mordant.

The most important transition metal ions in metal-complex dyes are chromium (coordination number = 6) and copper (coordination number = 4) and, to a much lesser extent, cobalt (coordination number = 6) and nickel (coordination number = 4). Chromium and cobalt complexes are particularly stable and therefore resist de-metallisation during application and use. The majority of the

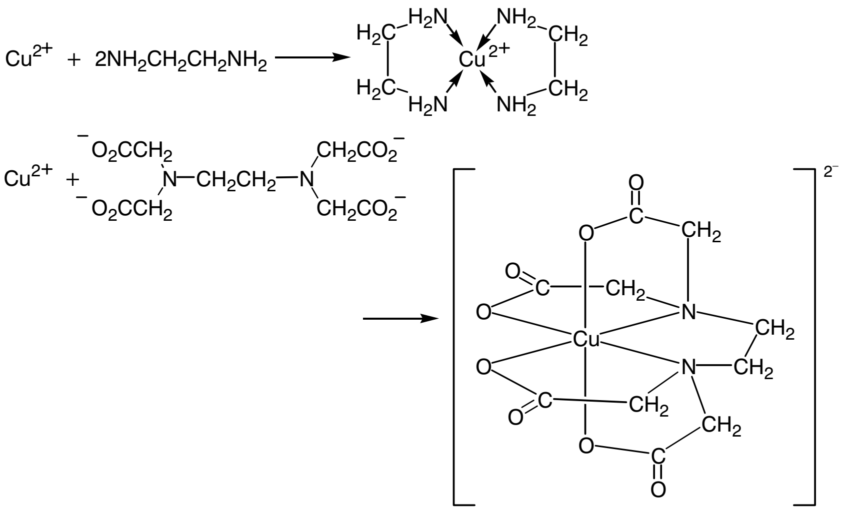
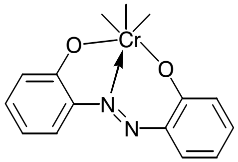
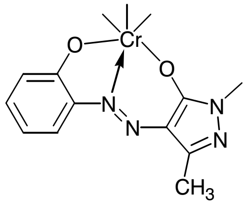
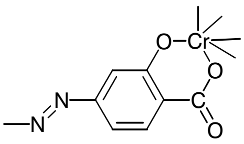


Figure 13.6 Chemical structures of complexes from polydentate ligands

dyes that act as ligands are tridentate. Examples include o,o′-dihydroxyazo, o-carboxy-o′-hydroxy-, and o-hydroxyarylazopyrazalone compounds (Figure 13.7). In some cases, the original ligand group in the dyestuff is a methoxy group, the methyl group being lost when the complex forms. Both salicylic acid or 1-hydroxyanthraquinone groups function as bidentate ligands and form chromium and copper complexes.


o,o′-Dihydroxyazo


o-Hydroxyazopyrazalone


o-Hydroxyarylcarboxylate

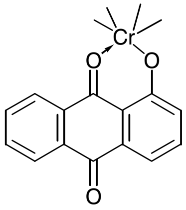
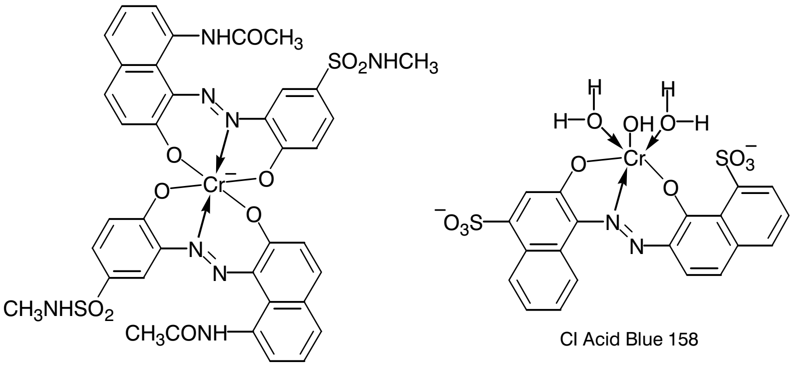

o-Hydroxyanthraquinone

Figure 13.7 Partial chemical structures of dye–metal complexes

The charge on the metal in a dye–metal complex is usually somewhat delocalised onto the electronegative atoms that surround it. The overall electric charge of a complex ion will depend on the charge of the original metal ion, the localised negative charge of sulphonate groups in the ligand dye molecule, and on any charge of additional monodentate ligands. Figure 13.8 gives some examples. It shows that complexes with chromium involve either one or two tridentate dye molecules and a single chromic ion. These are called 1:1 and 2:1 metal-complex dyes. In the latter, the two dye molecules may be identical or different.

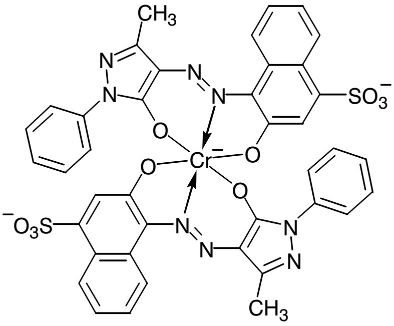
13.7.3 Acid mordant dyes for wool [1]

The most common mordant dyeing process today is the after-chrome process in which mordanting takes place after first dyeing the wool with an acid dye. The



CI Acid Black 60

CI Acid Blue 158



CI Acid Violet 90

Figure 13.8 Chemical structures of dye–metal complex dyes

oldest method of mordant dyeing, in which the material is mordanted before dyeing, and the metachrome process, in which the dye and chromium mordant are applied simultaneously to the wool, are obsolete.

Mordanting with chromium involves treatment of the dyed wool with sodium dichromate solution in the presence of a strong acid. Wool adsorbs the dichromate anions ($Cr_2O_7^{2-}$) by interaction with ammonium ion sites. The dichromate is then reduced to chromic ion (Cr^{3+}) (Scheme 13.10), oxidising cystine and other amino acid residues in the protein fibre. This oxidation of the wool causes a decrease in wet strength. Dichromate is used for wool chroming because it has reasonable substantivity and migration under the acidic conditions. It is, however, the chromic ion that forms the dye–metal complex. This cation has little substantivity for wool under acidic conditions and does not migrate because it binds strongly to carboxylate groups in the fibre. Dichromate adsorption increases with decreasing bath pH and its reduction to chromic ion consumes considerable amounts of acid (Scheme 13.10), increasing the pH of the bath, so there must be a high concentration of acid in the chroming bath.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Scheme 13.10

The after-chrome procedure is the most important for dyeing wool with mordant acid dyes. It has the advantage of requiring only a single bath. Dyeing is carried out with an acid dye, capable of forming a chromium complex, in the presence of acetic acid (3.0% owf) at the boil. Addition of formic acid completes exhaustion, if necessary. The exhausted bath is cooled to 75–80 °C, sodium dichromate added, and the bath reheated to boiling. It is important that the initial dyeing is level because the metallised dye is incapable of migration. Complete exhaustion of the dyebath before mordanting avoids any complexation in the solution. The pH of the chroming bath is 3.5–3.8 during the entire mordanting operation. At this pH, chromium is present mainly as dichromate rather than as chromate ion (CrO_4^{2-}) (Scheme 13.11).

$$2CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

Scheme 13.11

After-chroming usually gives a pronounced bathochromic shift in hue and the shades produced are usually dark and dull. A bathochromic shift involves an increase in the wavelength of maximum light absorption of the dye. This means that the colour shifts in the direction yellow–red–violet–blue–green (Chapter 1, Table 1.3). The final dyeing has very good washing and light fastness. Because of the pronounced change in hue on metal-complex formation, shading and colour matching are more difficult than in direct dyeing. Shading with small amounts of stable non-complexing dyes, such as milling, super-milling or 2:1 metal-complex dyes, does not jeopardise the washing fastness and brightens the rather dull shades of chrome dyes.

The significant increase in fastness to wet treatments that occurs on after-chroming the initial acid dye may be a consequence of the dye being chemically bonded to the fibre. This would involve carboxylate and amino groups in the wool acting as ligands and forming coordinate bonds to the metal in a 1:1 dye–metal complex. This has never been confirmed and it could not occur with 2:1 dye–metal complexes since all the coordination sites are full. The improved fastness to washing is therefore most likely due to the reduced solubility and diffusion of the complex because of the increase in molecular size on complexation, particularly for the formation of 2:1 dye–metal complexes.

The major problems with chrome dyes for wool are the long treatment time at the boil, which results in damage to the wool fibres, and the residual chromium in the dyehouse effluent. Dyeing at 80–90 °C, with added acetic acid, and after-chroming with sodium dichromate at around 90 °C, in the presence of formic acid and sodium thiosulphate, avoids detrimental effects on the quality of the wool cloth. The thiosulphate assists reduction of dichromate to chromic ion (Scheme 13.12). Fibre protective agents may also be added to the chroming bath. A minimum amount of dichromate in the after-chroming bath avoids excessive chromium in the effluent. Addition of thiosulphate ensures complete reduction to the less toxic chromic ion. In the past, the % owf of sodium dichromate for after-chroming would be half of the % owf of the applied dye. It is now substantially less. This minimises wool damage by oxidation and the effluent problem.

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \longrightarrow 2Cr^{3+} + 3S_4O_6^{2-} + 7H_2O}$$

Scheme 13.12

Chroming is best carried out at pH 3.5–3.8, using the manufacturer's recommended amount of sodium dichromate, and preferably in a fresh bath. Newer methods to reduce the chromium levels in the waste water include the use of chromic ion complexes with lactic acid. The proprietary chemical Lyocol CR (Clariant) contains a mild reducing agent and a complex chelating agent that binds chromic ion and exhausts it onto the wool. The newer methods for after-chroming, at low chromium levels, increase the risk of unlevel complexation and recommended procedures must be adhered to.

The tips of weathered wool fibres may have higher absorption of chromium than the roots and reduce dichromate to chromic ion more efficiently. Mordant dyes may therefore give differences in colour depth, or even two different hues, on the roots and tips of 'tippy' wool.

In the metachrome method, dyeing and mordanting the wool occur simultaneously, dyeing in the presence of sodium dichromate, ammonium sulphate and sodium sulphate at a pH around 6–7. Only a limited number of dyes are stable in hot solutions of dichromate and have reasonable substantivity at pH 6–7. The procedure has the advantage of facilitating shading and requires less time than the after-chrome procedure. It gives higher levels of residual chromium in the effluent. Only a few dyes of this type are now used (CI Mordant Brown 48) and the method is almost obsolete.

13.8 PRE-METALLISED METAL-COMPLEX DYES [4]

13.8.1 Chemical structures

Pre-metallised dyes are anionic 1:1 or 2:1 dye–metal complexes (Figure 13.8) used for dyeing wool and nylon under conditions typical of acid dyes. The properties of 1:1 and 2:1 metal-complex dyes resemble those of levelling and milling acid dyes, respectively. The fastness properties of both types on wool approach those of chrome dyes. Complexing a dye with chromic ion produces a bathochromic shift and dulls the shade. The dyeings are, however, slightly brighter than those of after-chromed mordant dyes. The dye–metal complex is pre-formed and stable. Hence, these dyes do not need any aftertreatment and are therefore much easier to use in colour matching.

In dyeing with all types of metal-complex dyes, soft water is preferred. If it is necessary to counteract any hardness, a polyphosphate sequestering agent is used rather than an EDTA type. The latter are capable of removing the metal from the dye–metal complex, thus liberating a non-metallised acid dye of different hue.

The 2:1 metal-complex dyes for wool, along with fibre-reactive dyes, are gradually replacing the other types of acid dyes, because of their superior fastness properties. Pre-formed metal-complex dyes are gradually replacing after-chrome dyes whose lengthy dyeing procedure tenders the wool, and which pose a serious environmental problem. With increasingly stringent surface water quality standards imposed by governments, there is now concern that dyeing with metal-complex dyes will have to be optimised to reduce chromium and cobalt levels in dyehouse waste water even further. If future water quality standards cannot be met, the use of metal-complex dyes will decline in favour of the metal-free fibre-reactive dyes for wool (Section 16.6).

13.8.2 Pre-metallised 1:1 dye–metal complex dyes

The Neolan dyes, originally introduced by Geigy in 1919, are 1:1 metal-complex dyes containing one atom of metal and one dye molecule with one or two sulphonate groups per dye molecule. Although the chromium complexes of those o,o′-dihydroxyazo dyes with only one sulphonate group would have no overall net electric charge, because the negative charges of two dissociated hydroxyl groups and one sulphonate group neutralise the positive charge on the original chromic ion, they behave as anionic dyes. This is because the residual positive charge on the chromium atom in the complex is somewhat delocalised while the sulphonate ion has a relatively localised negative charge. Alternatively, one of the non-dye ligands that completes the coordination of the central chromic ion may be a hydroxide ion rather than a water molecule or a neutral colourless ligand.

Dyeing wool with 1:1 metal-complex dyes involves a very acidic dyebath with sulphuric acid (pH 2) and possibly sodium sulphate. Without other dyeing assistants, the amount of concentrated sulphuric acid required is greater the higher the liquor ratio and the greater the amount of the dyes. It can easily reach 8% owf H_2SO_4. When dyeing with such high concentrations of sulphuric acid, there is a risk of hydrolytic damage to the wool fibres. Most manufacturers of these dyes now recommend dyeing methods with reduced amounts of sulphuric acid or the use of other acids such as formic acid. With lower concentrations of sulphuric acid (4–6% owf), a polyethyleneoxide levelling agent in the dyebath retards dyeing by complex formation with the dye. Alternatively, sulphamic acid can be used. At the boil, this hydrolyses to ammonium bisulphate and increases the bath pH from about 2.0 to 3.0–3.5, thus reducing fibre damage (Scheme 13.13). After dyeing, the residual acid in the goods must be neutralised or buffered using sodium acetate in the rinse.

$$NH_2{-}SO_3H + H_2O \longrightarrow NH_4^+ + HSO_4^-$$

Scheme 13.13

The Neolan P dyes (Ciba) are 1:1 dye–chromium complexes in which the coordination of the chromic ion is completed with colourless hexafluorosilicate ligands (SiF_6^{2-}). They only require 3–4% owf of concentrated formic acid at a pH of 3.5–4.0. This gives much less tendering of the wool compared to dyeing with high concentrations of sulphuric acid and eliminates the need for neutralising or buffering after dyeing.

A typical dyeing procedure for dyeing wool with 1:1 dye–metal complex dyes follows the scheme in Figure 13.2 but using 6% owf of sulphuric acid in the dyebath.

The fastness to washing of these dyes on wool is lower than for after-chrome dyes. It is comparable to that of fast acid dyes. Light fastness is usually good. These dyes are still important for dyeing loose wool, yarn for carpets, and for dyeing wool fabric after carbonising or acid milling, when the acid remaining in the goods serves directly for dyeing. It is unlikely that ligand groups in the wool bond to the 1:1 dye–metal complex since they have only moderate to good washing fastness and migrate readily under the acidic dyeing conditions. Because of this, the exhaustion is not optimal at pH 2. When applied at a higher pH of around 4, they give higher exhaustion, but produce skittery dyeings without a levelling agent. Their shades are often brighter than those of after-chrome dyes, but duller than those of non-metallised acid dyes. Shading and colour matching are relatively straightforward as there are no aftertreatments.

13.8.3 Pre-metallised 2:1 dye–metal complex dyes

These dyes have two dye molecules per metal atom and the molecular structures may be symmetrical, with two identical tridentate dye ligands, or unsymmetrical, with two different dyes. There are three types of 2:1 metal-complex dyes:

(1) weakly polar types that do not have sulphonate groups in the dye molecules. Their limited water solubility comes from polar methyl sulphone or alkylsulphonamide groups in the dye molecule. The complexes are anionic since the trivalent chromic ion reacts with four anionic ligand groups, such as the four hydroxyl groups from two o,o′-dihydroxyazo dyes;

(2) monosulphonated 2:1 dye–metal complexes that have an unsymmetrical structure since the two dye ligands are not identical and only one is monosulphonated;

(3) disulphonated 2:1 dye–metal complexes with symmetrical molecular structures since both identical dye ligands are monosulphonated.

The weakly polar 2:1 dye–metal complex dyes are applied to wool from a nearly neutral dyebath in the presence of ammonium acetate or sulphate. They require careful temperature and pH control since they have only limited levelling ability. In some cases, acetic acid may be added to the dyebath towards the end of dyeing. This decreases the pH to around 5.5 and promotes exhaustion. These dyes have very good light fastness and good washing fastness, but, for deep shades, the latter is lower than for dyeings with after-chrome dyes. They are used mainly on loose wool, slubbing, yarn and knit goods because they tend to highlight irregularities in woven materials. The 2:1 dye–metal complex dyes have high substantivity for wool, even in neutral solution. Dye levelling and penetration are usually good, provided that proprietary levelling agents are present in the dyebath. Uniformity of the initial fabric pH is critical and the goods are carefully neutralised after carbonising or other acidic processes.

The polar types usually have improved wet fastness compared to the weakly polar dyes, and have good light fastness. They can replace mordant dyes where there is a risk of damage to the wool from the extended boiling required in the after-chrome process. All the 2:1 dye–metal complex dyes have large molecules that tend to aggregate in solution and have slow diffusion in the wool fibre. The presence of sulphonate groups in the dye molecules leads to decreased substantivity in neutral solution, an indication of the importance of hydrophobic interactions in dyeing with the non-polar types. With increase in the degree of sulphonation, the dyeing pH must be lower to increase ionic interaction with ammonium ion sites in the wool fibre. The weakly polar dyes dye wool at pH 6–7 using ammonium acetate or sulphate in the dyebath, the monosulphonated dyes at pH 5–6 with ammonium acetate plus acetic acid, and the more polar disulphonated dyes at pH 4–5 using acetic acid. Dyeing is usually carried out at temperatures close to the boil, with careful control of the temperature during the heating phase. Alternatively, both low (80 °C) and high temperature (110 °C) dyeing methods are possible.

The disulphonated dyes possess the highest all-round fastness. The levelling capability of the disulphonated 2:1 complexes is poor, somewhat better for the monosulphonated type, and better still for the weakly polar dyes. The ability to migrate during dyeing increases with increasing dyeing pH and thus decreasing interaction with the diminishing number of ammonium ion sites in the wool. The dyes of lower migration therefore tend to give skittery dyeings and are not suitable for piece dyeing because of this.

All types of 2:1 metal-complex dye are suitable for dyeing shrink-resist wool from the Hercosett process (Section 7.4.2). Because of the cationic nature of the polymer deposited on the fibre surface and residual acid from the required pre-chlorination, strict control of the initial fabric pH and temperature are necessary to obtain level dyeings because of the greater substantivity of the dyes for the treated wool. An ester that slowly liberates an acid on hydrolysis, such as ethyl lactate, will gradually decrease the bath pH during dyeing (Scheme 13.4). To obtain optimum wet fastness in medium to heavy shades on shrink-resist wool, the dyeing may be aftertreated with a proprietary cationic agent. This presumably complexes with the anionic dye, reducing its solubility and diffusion capability.

Loose wool and slubbing can be dyed continuously by padding with metal-complex dyes, fixation usually being achieved by steaming. The pad bath contains wetting agents, a thickener to prevent drainage in the fibre mass since the solution pick-up is high (100–120%), as well as a variety of proprietary chemicals.

Coulombic interactions between dye anions and ammonium ion groups in the wool are important for determining the rate of dyeing and the degree of migration that is possible. As in the case of milling and super-milling acid dyes, the good washing fastness of metal-complex dyes, however, is more likely a consequence of hydrophobic interactions between the dye and the wool protein or between dye molecules themselves leading to aggregation of the dyes in the fibre.

13.8.4 Optimised acid dye ranges

A number of commercial dye ranges for wool are available in which the member dyes have a wide colour gamut and good compatibility. All the dyes have very similar dyeing and fastness properties. They have a common dyeing method despite being of several different types. The dyebath pH is around 4.5–5.0, close to the isoelectric region for wool. This minimises damage to the wool. Their high degree of exhaustion makes shade reproducibility much easier. Each range requires the use of a proprietary levelling agent that ensures good coverage of root and tip differences of the wool fibres. The dyes of the Sandolan MF (Clariant) range behave like fast acid dyes. For dyeings with good levelness, an acid release agent such as ethyl lactate is used in combination with a levelling agent. The Lanaset range (Ciba-Geigy) contains milling, reactive and 2:1 dye–metal complex dyes, whereas the Lanasan CF range (Clariant) has milling and 2:1 dye–metal complex dyes. The last two ranges give very good washing fastness.

13.9 DYEING NYLON WITH ACID DYES

13.9.1 Introduction

Nylon molecules have amino groups at the end of the polyamide chains. Nylon, like wool, can therefore be dyed with all types of acid dyes by an ion exchange process. Nylon filaments are sensitive to mechanical, thermal and chemical stresses during filament production as well as during their assembly into fabric and its preparation for finishing. These stresses modify both the chemical and physical structure of the nylon filaments and result in changes in dyeing rate and dye uptake. If the modification of the nylon is not uniform along the length of the filament, the final colour will be uneven. Disperse dyes, which dye most synthetic fibres, migrate readily when dyeing nylon and cover such chemical and physical irregularities in the filaments (Section 15.6). Unfortunately, the washing fastness of disperse dyes on nylon is only poor to moderate, particularly in heavy shades. They are used mainly for ladies' hosiery and lingerie. The washing fastness of non-metallised acid dyes on nylon is moderate to good and the light fastness is usually good. Milling or metal-complex dyes give dyeings of superior washing fastness on nylon. Their unlevel dyeing behaviour, however, results in poor coverage of filament irregularities. The 2:1 pre-metallised dyes, in particular, give dyeings of high light fastness, as required for example for nylon automotive fabrics. Besides hosiery and apparel, carpets are a major consumer of nylon, particularly in the USA, and are usually dyed with acid dyes.

13.9.2 Preparation of nylon before dyeing

Nylon filaments are relatively free from impurities. Scouring with a detergent and soda ash (Na_2CO_3) at 70 °C usually removes spin finishes and lubricants present on the filaments and any polyvinyl alcohol or other synthetic size on woven fabric. In some instances, where white nylon fabric has yellowed from overly severe heat setting (Section 13.9.3), bleaching with peracetic acid or sodium chlorite solution is possible. Compared to fabrics from natural fibres, the preparation of those from nylon is quite simple.

13.9.3 Heat setting

Nylon is a thermoplastic polymer. When treated in hot water, the temperature is well above the glass transition temperature (T_g) of nylon. Fabrics may give considerable changes in dimensions as filament tensions introduced during manufacture relax. Heat setting avoids fabric deformation and shrinkage provided that the temperature is higher than that to which the material will be subsequently exposed.

The full width fabric is heat set using a tenter frame. The separation of the chains holding the selvages, and the speed through the oven, define the final fabric width and length, respectively. On heating, intermolecular hydrogen bonds between amide groups break (Scheme 4.3) so that the polymer chains can move and adopt the positions required by the newly imposed dimensions without stress. At the setting temperature, new hydrogen bonds then form that stabilise the polymer structure. These new bonds are stable at temperatures up to the heat setting temperature at which they formed. They impart the required dimensional stability to the material.

Open-width fabrics are dry heat set at 190–215 °C for nylon 6.6, and 175–190 °C for nylon 6. Temperatures are lower for steam setting: 115–130 °C for nylon 6.6 and 110–120 °C for nylon 6. Since dry heat setting in hot air involves much higher temperatures than setting in steam, it involves a greater risk of polymer degradation. Dry setting sometimes results in yellowing of the material. Nylon hose are placed on shaped forms and heat set in a steam autoclave.

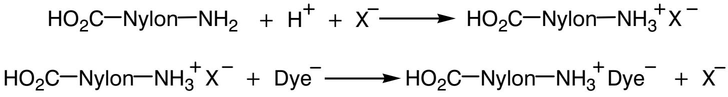
After dry heat setting in hot air at temperatures up to about 200 °C, the rates of dyeing of nylons 6.6 and 6 with both acid and disperse dyes decrease. This is mainly because of increased polymer orientation and crystallinity, but the number of polymer amino groups also decreases. Because of the decrease in dyeing rate and the risk of unlevel dyeing from non-uniform heat setting, it is preferable to heat set after dyeing, if this is possible. This requires a minimum level of dimensional stability at the maximum temperature of the dyeing process. Steam setting, however, increases dyeing rates with acid and disperse dyes. This latter process opens up the polymer structure making it more accessible to dyes.

13.9.4 Adsorption of acid dyes by nylon

The dyeing of nylon with acid dyes differs in a number of respects from that of wool. A simple ion exchange process (Scheme 13.14), similar to that for dyeing wool, explains many practical dyeing observations. The limited number of amino groups in nylon and its more hydrophobic nature, however, have a profound influence on its dyeing behaviour.

The amino group content of nylon is usually around 45 mmol kg^{-1} but can vary from about 15–20 up to 80–90 mmol kg^{-1} for different types. These values are much lower than the 820 mmol kg^{-1} for wool. In dyeing nylon at moderate acidity (pH 3–4), it is therefore relatively easy to saturate all the available ammonium ion sites with acid dye anions. The equilibrium molar adsorption of polysulphonated acid dyes is particularly low because of this. A simple acid dye with three sulphonate groups per molecule will neutralise the positive charge of all the available ammonium ion sites in the nylon at one third the molar quantity of a dye with a single sulphonate group. For a nylon with 45 mmol kg^{-1} of amino groups, the maximum dye adsorption of a trisulphonate dye is 15 mmol kg^{-1}. This corresponds to less than a 0.9 % owf dyeing for an acid dye with a molecular weight less than 600. The equilibrium molar dye adsorption at saturation of a polysulphonated acid dye of known molecular weight and purity is, in fact, a good method of determining the amino group content of the nylon. The limited number of ammonium ion sites in nylon, when dyeing with acid dyes under weakly acidic conditions, poses problems in dyeing deep shades. In particular, the production of blacks and other deep shades is problematic, since the amount of dye that saturates all the ammonium ion sites is insufficient to give the depth of colour required.

The non-polar environment inside nylon filaments, and the large separation between the amino and carboxyl groups, may not favour a zwitterionic form in nylon, as in wool, and absorption of acid probably involves protonation of free amino groups in a non-ionic polymer (Scheme 13.14).



$$HO_2C\text{—Nylon—}NH_2 + H^+ + X^- \longrightarrow HO_2C\text{—Nylon—}NH_3^+X^-$$

$$HO_2C\text{—Nylon—}NH_3^+X^- + Dye^- \longrightarrow HO_2C\text{—Nylon—}NH_3^+Dye^- + X^-$$

Scheme 13.14

Isotherms of the equilibrium adsorption as a function of pH for acid dyes of low substantivity (Figure 13.9) show that the dye initially interacts with ammonium ion groups in the nylon until these are all occupied at around pH 3. The shape of the isotherm resembles a titration curve. The amount of dye adsorbed depends on the acidity of the dyebath, which determines the number of ammonium ion sites. At low pH values, the nylon adsorbs additional dye beyond the saturation limit at pH 3. Under such acidic conditions, protonation of the carbonyl group oxygen atom of amide groups generates new cationic sites for dye adsorption. This also renders the amide group susceptible to hydrolysis at the elevated temperatures used in dyeing. Hydrolysis of an amide group forms a new amino group that, on protonation, can bind an additional dye anion (Scheme 13.15). In practice, dyeing

$$\text{—CH}_2\text{CH}_2\text{—NH—CO—CH}_2\text{CH}_2\text{—} + \text{H}^+ \longrightarrow \text{—CH}_2\text{CH}_2\text{—NH—}\overset{+}{\text{COH}}\text{—CH}_2\text{CH}_2\text{—}$$

$$\text{—CH}_2\text{CH}_2\text{—NH—}\overset{+}{\text{COH}}\text{—CH}_2\text{CH}_2\text{—} + \text{H}_2\text{O} \longrightarrow \text{—CH}_2\text{CH}_2\text{—NH}_3^+ + \text{HO}_2\text{C—CH}_2\text{CH}_2\text{—}$$

Scheme 13.15

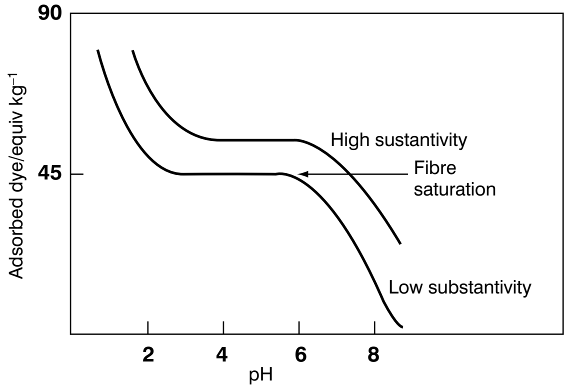


Figure 13.9 Equilibrium dye adsorption of nylon as a function of dyebath pH at constant temperature

below pH 2.5 is not possible because acid catalysed hydrolytic fibre degradation results in a loss of tensile strength.

Once a dye anion with moderate substantivity adsorbs onto an ammonium ion site in the nylon, it is quite resistant to displacement. A rapidly adsorbed dye anion can block a site and prevent adsorption of other dyes in the dyebath. The competition of acid dyes for the limited number of available dye sites can cause problems when dyeing with mixtures of incompatible dyes. Dyeing nylon with a mixture of the monosulphonated dye CI Acid Blue 47 and the disulphonated CI Acid Yellow 17 in acidic solution gives the expected green dyeing at low dye concentrations of 0.25% owf yellow and 0.17% owf blue, respectively. If dyeing is carried out using the same yellow to blue ratio but at higher dye concentrations of 1.5% owf yellow and 1.0% owf blue, however, the nylon is dyed yellow, most of the blue dye remaining in the bath. The yellow dye is more rapidly and more strongly adsorbed than the blue dye and is able to rapidly block the alkylammonium ion sites in the nylon. It will even displace any blue dye already adsorbed by the nylon. Many pairs of dyes exhibit this type of competition behaviour.

For milling dyes, which have higher substantivity for nylon, the isotherms showing the amount of dye adsorbed at equilibrium as a function of pH are similar to those for simple acid dyes, but displaced to higher pH values and with considerable dye adsorption above pH 7. Figure 13.9 shows an example.

As in the case of wool dyeing, the ion exchange mechanism is simple and useful. It does not, however, explain the pronounced substantivity of milling and metal-complex acid dyes in neutral solution, under conditions where the nylon only has very few ammonium ion groups. In the case of these types of acid dye, the dye–fibre interaction must involve forces other than the attraction of oppositely charged ions. Obviously, dipole–dipole and hydrophobic interactions between the dye and nylon molecules play an important role in determining the high substantivity and good washing fastness of these types of dyes.

Many of the high substantivity acid dyes, particularly hydrophobic monosulphonated or non-polar pre-metallised dyes, often dye nylon in amounts well over the amino group content, even at pH values as high as 6–7. Build up of deep shades is not a problem with such dyes. This phenomenon is called over-dyeing. In some cases, it has been shown that dyeing isotherms, giving the dye on the fibre as a function of the dye remaining in solution at equilibrium, are a combination of the Langmuir and Nernst isotherms. This behaviour corresponds to ion exchange up to saturation of the available cationic sites plus over-dyeing by solution of the dye in the nylon (Figure 13.10).

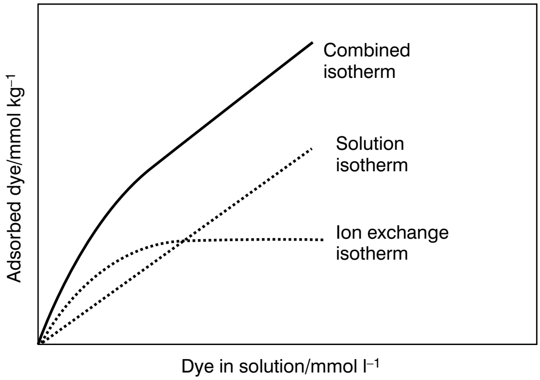


Figure 13.10 Adsorption isotherm for a metal–complex acid dye on nylon

The influence of temperature on the rate of acid dye absorption by nylon is complex. The glass transition temperature (T_g) of water-saturated nylon is probably not much greater than about 40 °C. Once the temperature exceeds T_g, the movement of polymer chain segments that is then possible should increase the rate of dye absorption as diffusion of dye molecules into the polymer matrix becomes easier. The temperature at which the initial rate of dyeing begins to significantly increase is called the dyeing transition temperature (T_D). This temperature, however, is often 20–30 °C higher than T_g under the given dyeing conditions. At temperatures somewhat higher than T_g, the voids between the chains in the amorphous polymer are too small to accommodate large dye molecules. Therefore, in spite of the increased mobility at temperatures above T_g resulting from easier polymer chain rotation, there is little dye absorption. Once the temperature exceeds the value of T_D, however, the greater ease of chain mobility creates voids whose average volume has increased to the point that allows dye molecules to enter them. The increasing size and mobility of these voids, now containing dye molecules, allows a significant increase in the rate of diffusion of dye into the polymer matrix.

13.9.5 Practical application of acid dyes to nylon

Many of the acid dyes used for dyeing nylon were first developed for dyeing wool and, like wool acid dyes, they are also classified according to their substantivity for nylon at a given dyeing pH. There are three main groups:

(1) low molecular weight dyes of low substantivity for nylon at pH 6–7. Although these dyes have good migration during dyeing, they require an acidic dyebath containing acetic or formic acid for good exhaustion;
(2) dyes that have moderate substantivity for nylon and good exhaustion when applied at pH 3–5 in the presence of acetic acid. These dyes have good fastness to washing on nylon;
(3) higher molecular weight dyes of high substantivity for nylon even in neutral solution. Dyeing is usually at pH 6.5–7.0 in the presence of ammonium acetate.

The substantivity of a given acid dye for nylon is invariably higher than for wool. Even when dyeing at the boil, the extent of dye migration when dyeing nylon will be less than for wool, but the dyed nylon will have better washing fastness. Monosulphonated acid dyes are preferred for dyeing nylon since their fibre saturation concentration is equal to the amino group content of the nylon and they build up to deeper shades better than polysulphonated dyes.

Dyeing of nylon with acid dyes starts at 40–50 °C in the presence of an appropriate acid, such as acetic acid or ammonium acetate depending on the substantivity. The temperature then gradually increases to the boil. Dyeing with weak acids is essential to avoid acid-catalysed hydrolysis and tendering of the nylon. The initial dyeing pH and the temperature gradient during the heating phase control the rate of exhaustion. The paler the shade being dyed, the higher the initial pH must be. At low concentrations of dye in the dyebath, a greater percentage of the total amount of dye present transfers to the fibre per unit time and the risk of unlevel dyeing is greater unless the bath circulation is very efficient. Many of the higher molecular weight dyes tend to exhaust very rapidly above a critical bath temperature (65–75 °C). This corresponds to the dyeing transition temperature, T_D. For this reason, the rate of heating is decreased in this temperature range. The dyebath may even be held at constant temperature for a while, around this critical value, before continued heating to the final dyeing temperature. For deep shades, addition of acetic acid, to decrease the bath pH, promotes better exhaustion as dyeing proceeds.

Despite the uniform appearance of continuous nylon filaments, they are often difficult to dye level. It is common to see paler filaments on a fabric surface where they have absorbed less dye than their neighbours. This effect is called barré. It arises from physical and chemical differences along the polymer filament, which influence both the dyeing rate and the total amount of absorbed dye. Unfortunately, many higher molecular weight acid dyes, which do not readily migrate, emphasise these irregularities giving filaments with different depths, and even hues. Uniform coverage of barré in nylon is just as difficult a problem as the level dyeing of ‘tippy’ wool. It is discussed in more detail in Section 13.9.6.

Auxiliary chemicals in the dyebath assist level dyeing, particularly for dyes of higher substantivity and poor migration. An anionic levelling agent present in the dyebath will block a number of ammonium ion sites in the fibres. This decreases the initial rate of dye adsorption and thus promotes level dyeing. If barré is likely to be a problem, the goods are run for some time in a heated bath with the required acid and anionic levelling agent before dye addition. The levelling agent anions exhaust onto the nylon, the bath is cooled and the dyes are then added to start the dyeing cycle. Too much anionic levelling agent causes excessive blocking and lowers dyebath exhaustion. Some levelling agents are cationic compounds, containing a non-ionic dispersant to prevent precipitation of the dye–auxiliary anion–cation complex. The formation of such a complex in solution retards exhaustion at low temperatures. The complex gradually dissociates as the temperature increases, liberating dye molecules that are then available for adsorption by the nylon (Scheme 13.5).

When dyeing nylon, acid dyes are often incompatible in mixtures. The dyes in a mixture must all have similar solubility and fastness properties. They will usually have the same number of sulphonate groups per dye molecule and give about the same rate of exhaustion. The dyeing will then always be on tone and there will be no hue change on repeated washing or light fading. The dyestuffs' suppliers recommend suitable trichromatic combinations.

Compatible dyes have about the same rate of exhaustion under the given conditions. Rates of exhaustion of individual dyes, however, may not always be a reliable guide to their dyeing behaviour in a mixture with other dyes. If a supplier's recommendations are not followed, selection of compatible dyes requires careful testing. The dyeing rate of a given acid dye often tends to be lower in the presence of other dyes. For example, CI Acid Violet 5 alone dyes nylon less rapidly than CI Acid Yellow 23 although both dyes are disulphonated. When dyeing with a mixture of these two dyes, under the same conditions, both dyes exhaust less rapidly, but now the violet dye adsorbs faster than the yellow. This may be related to the violet dye having a more extensive surface adsorption but a slower diffusion rate into the polymer than the yellow dye. Dyeing is never simple.

A number of direct cotton dyes are useful for dyeing nylon, particularly for deep shades. These are applied as acid dyes. They do not cover yarn irregularities well in pale shades but give reasonable fastness to light and washing.

The addition of benzyl alcohol to the dyebath (Irga-Solvent process, Ciba–Geigy) improves the coverage of barré and the washing fastness of the resulting dyeing. This process gives almost 100% exhaustion at lower temperatures (80–90 °C), in a shorter dyeing time. Re-use of the exhausted dyebath minimises the cost of the benzyl alcohol. Better levelling during nylon dyeing is also possible at temperatures above 100 °C using pressurised dyeing machines. Under these conditions, mild reducing agents such as thiourea in the dyebath scavenge oxygen that can oxidise amino groups in the nylon.

In most respects, the dyeing of nylon 6 with acid dyes resembles that of nylon 6.6. The washing out of the unreacted caprolactam monomer after filament spinning gives a more porous fibre that is easier to dye than nylon 6.6. Nylon 6 is more amorphous and has a lower melting point than nylon 6.6. It can be heat set at lower temperatures. The more open fibre structure and higher amino group content result in greater dye exhaustion rates, better dye build-up and better migration during dyeing with acid dyes. Dyeings of nylon 6, however, have somewhat lower washing fastness than those on nylon 6.6 when compared at the same depth of shade. When dyeing nylon 6 fabric at the boil, using a winch machine, permanent stretching of the fabric can occur. It may be necessary to use a lower dyeing temperature so the goods are less plastic.

To correct unlevel dyeings on nylon, the goods are treated at pH 8.0–8.5 at the boil. At this pH, there are few ammonium ion groups and some of the dye desorbs. The bath can then be acidified and the desorbed dye re-exhausted onto the nylon. This is less successful with high substantivity acid dyes. Chemical stripping requires the use of reducing agents such as sodium sulphoxylate-formaldehyde ($NaSO_2.CH_2OH$) but complete stripping may be difficult.

13.9.6 Barré

Barré is the visual difference in colour depth, and possibly of hue, along the length of dyed nylon filaments in a fabric caused by physical and chemical variations in the polymer. This gives a continuous pattern of colour stripes seen in the course direction in circular knits, as warp streaks in warp knits, or as weft or warp streaks in woven materials. Unfortunately, many acid dyes tend to accentuate barré, some dyes being more sensitive to chemical variations in the polymer filaments and others to physical variations. Filaments with chemical variations are more difficult to dye level.

Chemical irregularities in nylon filaments are mainly from a non-uniform distribution of the polymer amino groups, which causes variations in the rate of dye up-take and particularly the equilibrium dye content of the filaments. Polyamide formation is reversible and the amino group content may change as additional polycondensation or hydrolysis occur when the nylon is at high temperatures during processes such as heat setting or texturing. The number and distribution of amino groups may also vary because of their oxidation during processing.

Similar differences in dyeing rate along filaments come from variations in the degree of polymer orientation and crystallinity. These physical variations can arise from uneven treatment in processes such as filament drawing and texturising, fabric heat setting, and from uneven filament tensions during fabric construction and processing. Barré from physical variations in filaments can be minimised by using levelling acid dyes, or by promoting dye migration by dyeing above 100 °C, using an anti-oxidant such as thiourea to protect the amino end groups. Pretreating the goods with an anionic blocking agent before the acid dyes are in the dyebath is also a common method of promoting level dyeing. Lustre variations, arising from the effects of both filament surface and internal structure on light reflection and refraction, may also give a barré effect.

There are several dyeing tests for evaluating barré on nylon. Physical variations in the filaments influence the *rate* of dyeing, and chemical variations affect the *extent* of dyeing at equilibrium. Both types of barré may even be present in the same fabric, the rate of dyeing barré being more easily detected. Because of their good migration properties on nylon, disperse dyes, such as CI Disperse Blue 3, will uniformly cover most barré except that from gross physical variations in the filaments. When using acid dyes on nylon, those capable of migration will cover barré more uniformly. Unfortunately, these are the acid dyes of lower substantivity and lower fastness to washing. When deep shades are dyed to equilibrium, the amount of this type of adsorbed dye depends upon the number of ammonium ion sites. A trisulphonated acid dye such as CI Acid Red 18, applied to nylon at the boil in weakly acidic conditions, in sufficient concentration to saturate the fibre, will readily show if any variations in amino group content are present in the filaments. CI Acid Blue 45 (disulphonated), dyed to equilibrium under similar conditions, is also widely used for this purpose. Acid dyes of higher substantivity, such as CI Acid Blue 80 (disulphonated), will dye the more accessible filaments more rapidly and are useful for detecting physical variations in the filaments because of the poor migration under the dyeing conditions.

Pressure dyeing, dyeing with added benzyl alcohol, and dyeing with additions of levelling agents, all minimise barré. Pretreatment of the nylon material in a blank dyebath at a temperature around 85–90 °C, above the prevailing dyeing transition temperature, is also beneficial. Under these conditions, the movement of polymer chain segments allows the relaxation of tensions. This gives filaments with different chemical, thermal and mechanical histories time to equilibrate before dyeing takes place. A new dyeing process for nylon, developed by Du Pont and called the ‘Infinity’ process, uses this principle. The process involves running the goods in a blank bath containing the appropriate weak acid, at a constant temperature above the prevailing dyeing transition temperature, usually in the range 75–90 °C. The dye solution slowly runs into the bath over about 45 min using a metering pump. The conditions are such that the dye strike is so rapid that the actual concentration of dye in the bath is essentially zero during the entire dyeing operation. The name of the process comes from the condition of infinite exhaustion that prevails throughout dyeing. The rapid strike and poor dye migration result in yarns whose filaments are unevenly ring dyed on their exposed surfaces. This gives a higher colour yield than a well-penetrated dyeing. These ring dyeings show no decrease in washing, light and abrasion fastness when compared with well-penetrated dyeings at the same depth. By allowing the filaments to equilibrate by dyeing in a hot isothermal bath, barré is much less of a problem using this dyeing method.

13.9.7 Back-tanning

Many of the simple but brightly coloured acid dyes give dyeings on nylon of only moderate fastness to washing, particularly for deep shades. The washing fastness of such dyeings improves on aftertreatment of the dyed nylon with a solution of tannic acid containing formic acid at 90 °C (70 °C for nylon 6). This is done using a fresh bath. The anionic tannic acid is adsorbed onto the nylon surface by attraction to the cationic ammonium ion groups at the ends of the polymer chains. Subsequent treatment with a solution of tartar emetic (potassium antimonyl tartrate, $KSbOC_4H_4O_6$) produces a film of the insoluble antimony salt of tannic acid all around the filament surface. It is this film that limits desorption of the dyes during subsequent washing. When using low liquor ratio dyeing machines, a fresh bath for the tartar emetic solution avoids precipitation of the antimony salt of tannic acid in the liquor.

This so-called full back-tanning aftertreatment gives a somewhat stiffer, slightly yellower fabric but with improved colour fastness to washing. The process has, however, a number of disadvantages:

(1) antimony salts are poisonous and pose an environmental threat;
(2) the process is time-consuming, since ideally two separate baths are required after dyeing;
(3) yellow-brown impurities in commercial grade tannic acid dull the shade;
(4) tannic acid tends to discolour under alkaline washing conditions.

Because of the dulling and yellowing effect on the hue, back-tanning is limited to deep dyeings that tend to have poor washing fastness without this aftertreatment. The improvement in washing fastness obtained by back-tanning is lost if the fabric is heat set after dyeing, using either hot air or steam, as these processes rupture or even remove the surface film.

Because the back-tanning process is expensive and environmentally unsound, cheaper synthetic chemicals for this purpose were developed [5]. They are called synthetic tanning agents or syntans. These are colourless, anionic, water-soluble polymers formed by condensation of formaldehyde with phenol, naphthol, or hydroxybiphenylsulphone sulphonic acids or their mixtures. Commercial syntans are complex polymeric mixtures. The average molecular weight must be as high as possible while still allowing solubility in water. Syntans are applied to dyed nylon at 80 °C at around pH 4 using acetic or formic acid in the bath. Although direct syntan aftertreatment in the exhausted dyebath is possible, a fresh bath is desirable.

The anionic syntans do not form a skin like the tannic acid/tartar emetic combination. In acidic solution, the syntan is substantive to nylon. The molecules adsorb on the filament surface by interaction with ammonium ion sites in the nylon but, because of their molecular size, they cannot penetrate far into the polymer. The layer of adsorbed syntan polymer molecules on the nylon surface presents a considerable barrier to dye transfer in either direction. They therefore improve the washing fastness of the dyeing but their presence also prevents dye penetration. Syntans are therefore useful for preventing absorption of direct dyes by nylon when dyeing cotton/nylon blends with direct cotton dyes. The improvement of the washing fastness of nylon fabrics dyed with acid dyes obtained by syntan aftertreatment is somewhat less than that of the full back-tanning process. Syntans, however, have little or no influence on the hue of the dyeing although they may slightly reduce the light fastness.

13.10 DYEING NYLON WITH METALLISED DYES

13.10.1 Mordant dyes

Nylon can be dyed with acid dyes suitable for after-chroming. Dyeing is usually at the boil using ammonium acetate or small amounts of acetic acid. After-chroming in the exhausted dyebath reduces water and steam consumption. If complexation of the dye occurs in the solution, there is a risk of deposition of the less soluble metallised dye on the nylon surface. This deposit decreases the fastness to perspiration and rubbing. To complete exhaustion, some additional acid may therefore be needed towards the end of the dyeing process. This generates more ammonium ion sites in the nylon and promotes further dye adsorption. If the extent of dyebath exhaustion is not adequate, a fresh bath is necessary for after-chroming.

Nylon, unlike wool, contains few groups capable of reducing sodium dichromate to chromic ion, the form required for complex formation with the dye. A reducing agent such as sodium thiosulphate is effective (Scheme 3.12). After-chroming is carried out at the boil using sodium dichromate and formic acid. The sodium thiosulphate is added once most of the dichromate anions have adsorbed onto the nylon. The reduction process is much slower than for wool. Efficient after-chroming of dyed nylon at 130 °C is possible without added thiosulphate. It is likely that formic acid reduces the dichromate under these conditions. Residual dichromate, left in the nylon, promotes tendering on exposure to light. Therefore, complete reduction of dichromate to chromic ion and effective complexation with the dye are essential. Despite the good fastness to washing and light of the after-chromed dyeings on nylon, this dyeing process is now restricted mainly to blacks. The after-chrome process makes shade correction and colour matching much more difficult because of the pronounced change in hue that occurs.

13.10.2 Metal-complex dyes

The dyeing characteristics of pre-metallised dyes vary widely depending on the type of metal-complex dye and on the molecular complexity and degree of sulphonation. Like all acid dyes, their application to nylon involves the usual problems:

(1) competition for the available ammonium ion sites in the nylon and exclusion of the less substantive dyes;
(2) difficulties in producing deep shades because of the limited number of available ammonium ion sites in nylon;
(3) poor migration and levelling during dyeing, which accentuate barré.

The 2:1 metal-complex dyes have very good light fastness in pale shades and good washing fastness, even in deep shades. Many weakly polar 2:1 dye–metal complex dyes, particularly those without sulphonate groups in the dye ligands, have good build-up properties on nylon, because of over-dyeing (Section 13.9.4). In deep shades, they absorb in amounts exceeding the amino group content of the nylon and therefore must interact with the fibre by forces other than ionic forces. They do not therefore give blocking effects. Most 2:1 dye–metal complexes, however, accentuate physical irregularities in the nylon filaments and cause barré. Dyeing with either a weakly dye-complexing (cationic) or site-blocking (anionic) auxiliary levelling agent in the dyebath overcomes this problem. Alternatively, dyeing at

120 °C (110 °C for nylon 6), in the presence of an anti-oxidant to avoid amino group oxidation, promotes better levelling.

The 2:1 pre-metallised dyes have poor migration during dyeing of nylon, and level dyeing requires good control of the dyeing process. Dyeing is usually started at pH 7. The goods are pretreated with a suitable levelling agent and ammonium sulphate. The dyes are added and the temperature raised to the boil. Some dyes may have very rapid strike at 60–70 °C. A decreased rate of heating in this temperature range lowers the risk of unlevel dyeing.

The very acidic dyebaths used in wool dyeing with 1:1 dye–metal complex dyes will cause hydrolysis of the nylon. Some dyes of this type will dye nylon using acetic acid at pH 4–6 with a weakly cationic levelling agent. They give dyeings of good washing and light fastness.

13.11 LIGHT AND OZONE FADING OF ACID DYED NYLON

Nylon fabrics dyed with acid dyes generally have moderate to good light fastness. All auxiliary chemicals used in dyeing or for aftertreatments should be tested to ensure that any residue left in the fabric does not decrease the fastness to light. This also applies to ozone fastness. Ozone is a major constituent of polluted urban air and is a powerful oxidising agent capable of rapidly destroying the colour of many types of dyes.

Nylon is a major fibre for production of automotive fabrics and carpets because of its superior properties. It is, however, becoming increasingly difficult to meet the car manufacturers' demands for light fastness ratings of 6 (Section 24.3.4) or even higher. Some nylon fabrics are aftertreated with copper derivatives (1–2% owf) to improve their fading resistance but with the increased risk of environmental contamination by copper. Automotive carpets and fabrics are often aftertreated with colourless ultraviolet photostabilisers. These strongly absorb ultraviolet light on the nylon surface and protect both the fibre and the dyes in it from photodegradation. The light fastness is therefore better. These chemicals function like sun screen products, the absorbed ultraviolet light being converted into heat. For automotive interior fabrics and carpets, the UV stabilisers do not need to have any significant degree of washing fastness but they must be colourless, odourless and non allergenic.

The fading of the colour of dyed nylon by ozone in industrial environments is a surface phenomenon. The fastness to ozone is therefore lower for dyeings that have poor dye penetration into the filaments. The ozone fastness, however, increases with increase in the extent of dye–fibre interaction. For dyes with the same chromophore, the ozone fastness on nylon increases in the following order: disperse dye, disulphonated acid dye, monosulphonated acid dye, and reactive dye. Unfortunately, even reactive dyes (Chapter 16) cannot meet the ozone fastness demanded for automotive carpeting. Testing of ozone fading is not easy but is necessary because there is no relation between colour fading by ozone and by light.

13.12 NYLON CARPET DYEING

Manufacture of tufted carpets consumes large quantities of nylon multi-filament yarn. Modern filaments often have unusual properties compared to the original cylindrical nylon filaments. They may have trilobal cross-sections that hide dirt more effectively, and even conductive surfaces or cores that effectively dissipate static electricity. In addition, fluorocarbon finishes reduce soiling, stain blockers hinder penetration of anionic colorants in spilled food and drink, while ultraviolet photostabilisers improve the stability of the both the nylon and the dyes present towards light.

Considerable quantities of wide, tufted nylon carpeting are dyed continuously, particularly in the USA. The nylon filament yarn is textured to give it bulk, and heat set before tufting using dry heat or steam. Tufting involves punching of the multi-filament yarn through the primary backing and forming and tying of the filament loops. These may or may not be cut to form the pile.

13.12.1 Continuous dyeing of nylon carpets with acid dyes

For large quantities of carpet in a single colour, continuous dyeing is by far the most economic method of coloration. Great lengths of evenly dyed carpet, up to 12 m wide, require even dye application and fixation. Before application of the dye solution, the carpet is often well wetted with a solution of a wetting agent such as disodium di-octylsulphosuccinate. Steam set yarns are much easier to dye than dry set yarns. Addition of gum to the wetting agent solution promotes uniform wetting and helps to eliminate ‘frostiness’ at the pile surface caused by the migration of the dye away from the fibre tips during steaming. The pre-wetted carpet may be vacuum extracted before dye application. A high pick-up (300–400%) of thickened dye solution is run onto the pile surface across the full carpet width. A variety of systems are available for this step. Pre-wetting avoids pools of dye solution on the pile surface that run into pools on the carpet backing. A carpet of weight 1.0 kg m^{-2}, 12 m wide, moving at 20 m min^{-1} with a 300% pick-up of dye solution, requires 720 kg min^{-1} of dye solution. Liquid acid dyes are necessary for rapid preparation of solutions by simple dilution. Dye solution may also be applied continuously to dry carpet, in which case wetting agents are in the dye solution. By using separated streams of different dye solutions, various multi-colour effects are possible (Section 23.9).

The wet carpet is then steamed for 3–5 min, preferably in dry saturated steam at 100 °C. If dye penetration into the fibres during steaming is not adequate, the colour fastness properties may be inferior, particularly the ozone fastness. The latter can increase from 2–3 up to 4–5 as the steaming time increases and the dyes penetrate deeper into the filament interior. Finally, washing the carpet removes unfixed dyes, residual gum and auxiliary chemicals. When only small lots of carpet are involved, dyeing is carried out using winch machines.

13.12.2 Stain blockers [6]

Stain blockers improve the stain resistance of nylon carpets towards anionic dyes in spilled food and drink. The original stain blockers were of low substantivity and the appreciable amounts remaining in the bath increased the BOD problems of the effluent (Section 8.5.1). They also turned yellowish on light exposure. A pale blue carpet would therefore become greener in the exposed areas. Current formulations include the stain blocker and fluorocarbon polymers, and are more stable. The fluorocarbon polymer forms a film on the nylon surface that resists the spreading of both oil and water and to which particles of dirt do not adhere readily. The build-up of static electricity is also reduced. Stain blockers are anionic polymers similar to the syntans used for the aftertreatment of nylon dyed with acid dyes (Figure 13.11). Because of their anionic nature, they repel the anionic colorants in spilled foods and the polymer film on the surface of the nylon fibres provides a physical barrier to the penetration of non-ionic materials.

The fluorocarbon polymer and stain blocker are usually applied after dyeing since they interfere with dye fixation. Application procedures and conditions depend upon the particular products selected. Continuous application of the stain blocker, by spray, foam, or liquid jet, to the wet carpet after continuous dyeing is common. The lack of colour of these products requires extra care to ensure their uniform application for the best performance in use. The dispersion contains stain blocker, magnesium sulphate and fluorocarbon polymer. Acids such as acetic, formic, citric, or sulphamic acid will give a pH of 2.0–4.5, depending upon the

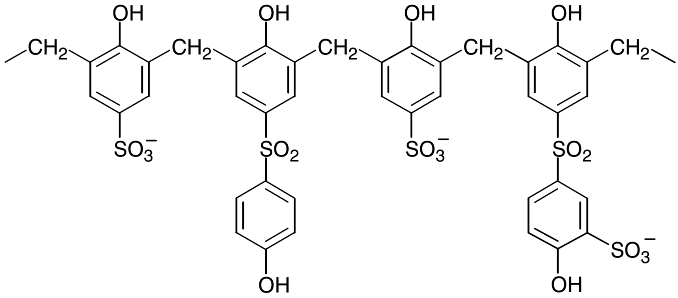


Figure 13.11 Partial chemical structure of a stain blocker

product selected, the nylon type and heat setting method used. The carpet is then steamed. The magnesium ions lower the aqueous solubility of the anionic stain blocker thus favouring transfer to the filament and the formation of an insoluble polymer film on the surface. Hydrogen bonds between the hydroxyl groups of the stain blocker molecules and amide groups in the nylon hold it onto the fibre surface. This is augmented by coulombic attraction between the blocker's sulphonate groups and ammonium ion groups in the nylon surface. This promotes substantivity of the stain blocker for the nylon but its molecular size prevents penetration into the polymer.

Treated carpets have good water resistance, in the absence of surfactants. If water penetrates into the nylon fibres, coloured anions will not. The anionic layer of polymer blocker on and just inside the nylon surface repels them. Excessive steaming may cause a loss of the stain blocking effect if the polymer diffuses too far into the nylon. The degree of penetration is clearly less, the higher the molecular weight of the polymer. Stain blockers offer no resistance to non-ionic stains such as those from coffee and mustard. They also interact strongly with cationic chemicals found in some cleaners and creams. The use of anionic stain blockers on nylon carpets has increased dramatically despite their far from ideal performance. Some would claim that their market success involves more consumer persuasion than consumer demand.

13.13 DYEING MODIFIED NYLONS

There are a number of modified nylon polymers available having different substantivities for both acid and basic dyes (Section 4.2.4). Light dyeing, normal dyeing, deep dyeing and ultra deep dyeing types are available for dyeing with acid dyes. These have increasing amino group contents, respectively, but all dye to the same depth with disperse dyes. In addition, there are also basic dyeing varieties of nylon, containing anionic groups capable of binding cationic dyes (Section 4.2.4). Mixtures of different nylon types in a carpet give attractive tone-in-tone and multi-colour effects because of their differential dyeing behaviour.

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CHAPTER 14

Dyeing cellulosic fibres with direct dyes

14.1 INTRODUCTION

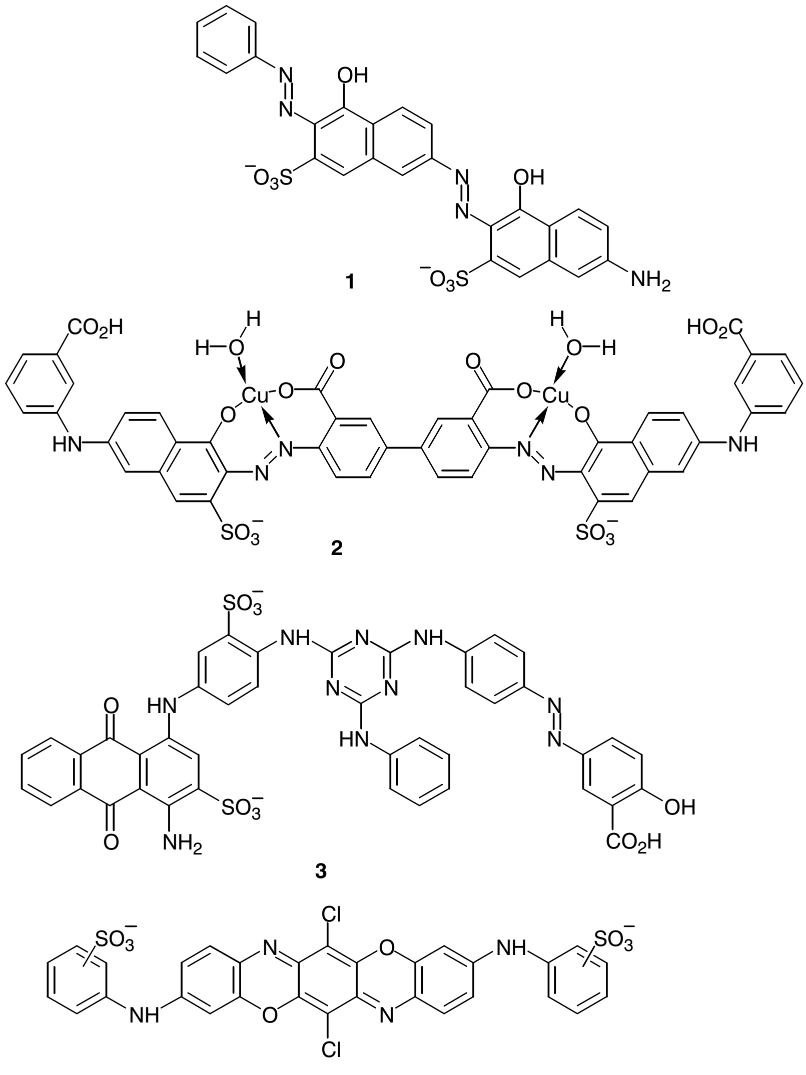
Direct cotton dyes have inherent substantivity for cotton, and for other cellulosic fibres. Their aqueous solutions dye cotton usually in the presence of an electrolyte such as NaCl or Na_2SO_4. Direct dyes do not require the use of a mordant and, as their name implies, the dyeing procedure is quite simple. The goods go into the bath followed by the dissolved dyes. The bath is then gradually heated, usually to the boil, and additions of salt promote dyeing.

Many direct dyes are relatively inexpensive. They are available in a full range of hues but are not noted for their colour brilliance. Their major drawback is their poor to moderate fastness to washing. This limits their use to materials where good washing fastness is not critical. The light fastness of dyeings with direct dyes on cellulosic fibres varies from poor to fairly good, although some copper complex direct dyes have very good light fastness. As usual, the deeper the colour of the dyeing, the lower the fastness to wet treatments, and the higher the fastness to light. Various aftertreatments of the dyeings improve the fastness to washing. In some cases, however, such aftertreatments decrease the light fastness. They also invariably cause a change in hue that makes shade correction and colour matching more difficult.

Cotton, and other cellulosic fibres, are dyed with direct, sulphur, vat, reactive or azoic dyes – more types than for any other fibre. Each of these classes of dye has its own application methods, dyeing characteristics, cost, fastness properties and colour range, and therefore its own particular advantages and disadvantages. Within each group, application and performance properties vary considerably so the choice of which dyes to use is often not easy. Direct dyes generally cannot meet today's more stringent washing fastness requirements for apparel and linens. In recent years, their share of the market has gradually declined in favour of reactive dyes. The latter have very good washing fastness on cellulosic materials and often have bright colours.

14.2 CHEMICAL CONSTITUTIONS OF DIRECT DYES

Sulphonated azo dyes constitute the predominant group of direct dyes (**1**, in Figure 14.1). These are usually bis-, tris-, or tetra-azo compounds, the latter type often being brown and black. Direct dyes usually have long, coplanar molecular



1

2

3

4

Figure 14.1 Constitutions of typical direct dyes. **1**, CI Direct Red 16 (27680); **2**, CI Direct Blue 93 (22810); **3**, CI Direct Green 28 (14155); **4**, CI Direct Blue 106 (51300) structures. In general, the greater the extent of conjugation, the longer the wavelength of maximum light absorption. Green dyes must have two absorption bands in the red and violet regions of the visible spectrum. Green polyazo direct dyes, however, tend to be dull and bluish in hue. Bright green direct dyes have blue and yellow dye structures bonded together by a linking group that prevents their mutual conjugation (**3**, in Figure 14.1).

There are some yellow and orange stilbene direct dyes obtained from condensation reactions of 4-nitrotoluene-2-sulphonic acid. These are often of unknown constitution but have stilbene, azo and azoxy groups. Sulphonated copper phthalocyanines give turquoise direct dyes. These have good light fastness, but low wet fastness and poor colour build-up. A number of blue dyes based on the triphenodioxazine structure (**4**, in Figure 14.1) have good fastness to light. There are also some pre-metallised azo copper complexes that give dyeings of very good light fastness (**2**, in Figure 14.1).

Many of the older azo direct dyes based on benzidine and its derivatives, such as Congo Red (Figure 1.3), and some made from 2-naphthylamine, are no longer manufactured in many countries. Benzidine and 2-naphthylamine are proven carcinogens.

Although direct dyes often have similar structures to acid dyes, they generally have higher molecular weights and extended coplanar molecular structures. There is, however, no clear demarcation between acid and direct dyes. Some direct dyes dye protein and nylon fibres just as a few acid dyes will also dye cotton.

14.3 DYEING PROPERTIES OF DIRECT DYES

14.3.1 Classification according to dyeing characteristics

Classification of direct dyes according to their chemical structures is not of much use to the dyer since dyes with similar chemical constitutions can have quite different application and fastness properties. Direct dyes vary widely in their dyeing behaviour giving compatibility problems. Grouping of direct dyes according to their dyeing properties is therefore more useful. The most common classification of direct dyes is that of the Society of Dyers and Colourists (SDC), based on their levelling ability and their response to increase in the dyeing temperature and to added salt during exhaust dyeing.

(1) **SDC Class A direct dyes.** These are self-levelling dyes with good migration, even in the presence of salt. They usually require considerable amounts of salt for good exhaustion because of their lower substantivity. These dyes are relatively low molecular weight mono- and bis-azo dyes with several anionic sulphonate groups per molecule. They therefore have good water-solubility and do not aggregate to a significant degree in solution. Dyeing is started at 50 °C in the presence of added salt, the bath heated to the boil over 30–40 min, and dyeing continued at the boil for up to an hour. Several further salt additions, of increasing size, are required to promote exhaustion, the total amount of salt (5–20% owf NaCl) depending upon the depth of shade and the liquor ratio. Although these dyes would give greater exhaustion by dyeing at lower temperatures, dyeing at the boil allows good levelling and adequate penetration of the dyes into the fibre.

(2) **SDC Class B direct dyes.** These are salt-sensitive or salt-controllable dyes, with poor levelling characteristics. They are of higher molecular weight than Class A dyes, often bis- and tris-azo dyes with just a few sulphonate groups per molecule. They have low to moderate substantivity in the absence of salt but give much increased exhaustion on addition of small amounts of salt to the dyebath. The dyeing method is the same as for Class A dyes but the initial salt is omitted. Gradual addition of dissolved salt, at the boil, controls the exhaustion.

(3) **SDC Class C direct dyes.** These very salt-sensitive dyes exhibit poor migration. Level dyeing depends on the gradual increase of the dyeing temperature and subsequent additions of limited amounts of salt. Levelling agents may be required. These dyes are temperature-controllable. Dyeing is started at low temperature without added salt. The bath is slowly heated, with particular care in the temperature region where exhaustion is most rapid. Some salt may be added during further dyeing at the boil. These dyes are often polyazo dyes with few sulphonate groups and of high substantivity for cellulose. At lower dyeing temperatures, they are very prone to aggregation in solution and sensitive to salt addition. Salt in the dyebath impedes exhaustion at low temperatures because it promotes even more aggregation. The higher the degree of aggregation of the dye, the lower the concentration of individual dye molecules in the solution that can diffuse into the fibre, and therefore the lower the rate of dyeing. Dye aggregates are too large to penetrate into the pores of cellulosic fibres.

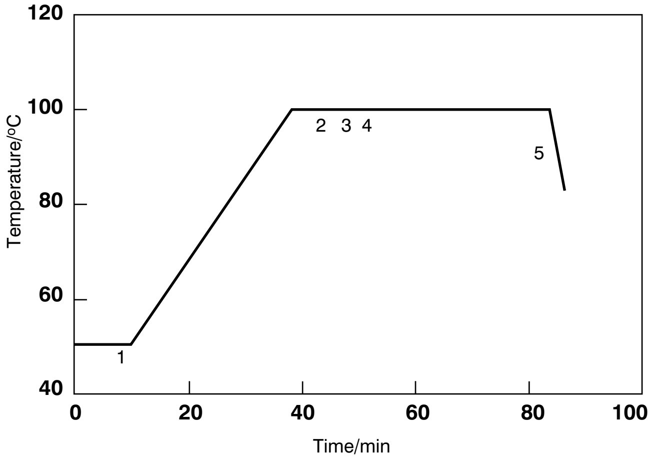
The SDC classification tests involve dyeing trials using a 30:1 liquor ratio. A migration test and a salt sensitivity test are carried out using the dyes under examination along with standard dyes for comparison [1,2]. The migration test (Section 10.4.5) is conducted at the boil in the presence of 10% owf salt using a dyeing of the test dye along with an equal weight of undyed cotton. Dyes that exhibit good migration, comparable to that of the standard dyes, belong to Class A. For the other dyes showing poor migration ability, a salt sensitivity test is carried out. Dyeings are prepared at the boil in the presence of 0.6, 0.8 and 1.0% owf salt for 30 min. The dyed samples are removed and replaced with the same weight of undyed material, further salt is added to give a total of 20% owf NaCl and dyeing continued for another 30 min. For Class B dyes, the initially removed samples, dyed at low salt concentrations, are lighter or the same as the second samples dyed in the presence of additional salt. For Class C dyes, the initial dyeings are darker than the later ones.

An examination of the molecular structures of direct dyes from the three groups, shows that in passing from Group A to Group C, dye substantivity generally increases because of increased molecular weight and a lower number of sulphonate groups per dye molecule. Class C dyes therefore generally have better washing fastness than Class B dyes, with Class A dyes having even lower fastness.

Despite its value, the SDC classification is not readily applicable to dyeing at low liquor ratios as in jet, jig or pad dyeing. In these cases, a strike test may be a more useful indicator for selecting compatible dyes (Section 14.3.4). At low liquor ratios, dye aggregation is more pronounced since the dye solution is more concentrated for a given % dye owf. SDC Class B direct dyes may then require temperature control as well as salt control to obtain level dyeings.

14.3.2 Introduction to dyeing methods

The selection of specific direct dyes for dyeing cellulosic fibres depends on their dyeing properties, the particular fastness requirements, any aftertreatments used to improve the washing fastness, and on the particular finishing processes involved. Possible staining of other fibres present in the material by the direct dyes is another consideration. Dyeing with direct dyes is carried out in neutral solution. The dyebath is gradually heated to promote diffusion and levelling of the dyes, usually with gradual salt addition to exhaust the dyebath. Figure 14.2 illustrates a typical dyeing procedure.



1 Add dyes
2 Add 20% of total salt
3 Add 30% of total salt
4 Add 50% of total salt (final concn 10 g l^{-1})
5 Rinse

Figure 14.2 A typical dyeing process for a Class B direct dye on cotton

Dyeing liquor ratios range from about 30:1 for open loose fibre machines, through 20:1 for winch dyeing, 5:1 for jet and package machines, to less than 1:1 in jig dyeing and padding. Direct dyes usually have good water solubility but the solubility is lower in the presence of salt. At low liquor ratios and temperatures, limited dye solubility may become critical when dyeing deep shades. Any undissolved particles of dye that touch the fabric surface will usually give a dark coloured spot. The dye solution is prepared by pouring boiling water onto an aqueous paste of the dye, prepared with some wetting agent if the powder is difficult to wet. Some dyes require soft water to avoid precipitation of the calcium and magnesium salts of the sulphonated dyes. Others give salts or complexes of different hue with metals such as iron and copper that are sometimes present in the water supply. A sequestering agent such as EDTA (Section 8.3.3) will bind unwanted metal ions and prevent the above problems. Sodium hexametaphosphate is the preferred sequestrant when using copper complex dyes. Agents such as EDTA remove the copper ion from the metal-complex dye giving the very stable EDTA–copper complex and freeing the non-metallised dye that usually has a different hue.

Levelling agents are useful when using dyes that do not easily migrate. These are surfactants, or mixtures of surfactants, based on non-ionic polyethylene oxides and may also contain cationic agents. These chemicals form complexes with many types of anionic dyes, including direct dyes. Complex formation at relatively low temperatures reduces the concentration of the free dye in the bath so that the rate of dyeing is reduced. The dye–auxiliary complex molecule is too large to penetrate into the fibres' pores. The surfactants in these products disperse the dye–auxiliary complex and prevent its precipitation. As the dyeing temperature increases, the dye–auxiliary complex gradually breaks up, liberating more free dye, which is then available for dyeing. In this way, the rate of temperature increase controls the rate of exhaustion, giving dyeing with improved levelness.

High dyeing temperatures for cellulosic fibres give much better dye migration, smaller risk of unlevelness and better fibre penetration. The SDC Class B and C dyes migrate better at 120 °C, although the dyebath exhaustion is usually lower at this temperature. Decreasing the dyeing temperature towards the end of the process, once the dyeing is level, will then improve the exhaustion. At 120 °C, however, there is a greater risk of dye decomposition or azo dye reduction by the cellulose. Dyes must therefore be selected with care.

Scouring and bleaching of cotton consume large amounts of steam and hot water. Because of increasing energy costs, many dyehouses dye grey cotton and cotton/polyester fabric in a combined scouring and dyeing process, provided this gives satisfactory results. This is possible for dull and deep shades on some knitted materials, where the major contaminant to be removed is the lubricating oil used in knitting. For a brighter hue, it is usual to simultaneously scour and dye the goods, and then to add hydrogen peroxide and alkali to the exhausted dyebath and bleach at 80–90 °C. This is called post-bleaching. In this way, the bath is heated only once, minimising steam consumption. Dye suppliers recommend dyes for these types of combined processes that are stable to alkali and resist fading during post-bleaching.

Problems with tailing arise in padding with solutions of direct dyes because of the inherent substantivity of these dyes for cellulose (Section 10.5.2). To minimise this, the selected dyes should have low, comparable strike rates. Padding may be carried out at higher temperatures in the range 50–90 °C, with dye solution containing a minimum of salt, to reduce the substantivity. SDC Class A direct dyes tend to migrate during drying and steaming and Class C dyes have rapid strike and give most tailing. Class B dyes are therefore often the best choice for continuous dyeing. Dyes of widely differing substantivity obviously cannot be applied together by padding.

The major pad dyeing processes are:

(1) pad with dye solution, dry, pad with salt solution, steam;
(2) pad with dye solution, steam;
(3) pad with salt solution, pad wet-on-wet with dye solution, steam.

Cotton/polyester materials can be continuously dyed by padding with combinations of direct and disperse dyes.

Stripping of dyeings with direct dyes is possible by hypochlorite (NaOCl) or dithionite ($Na_2S_2O_4$) bleaching, which destroys the dye on the fibre by oxidation or reduction, respectively. This is more difficult with aftertreated dyeings. Cationic aftertreatment agents must be removed from the stripped goods with formic acid since they influence re-dyeing. Copper complexes can be demetallised by treatment with EDTA, usually giving a paler shade, and then stripped or re-dyed.

14.3.3 Problems in batch dyeing with direct dyes

A number of problems can complicate the dyeing of cellulosic fibres with direct dyes. The residual chlorine in the fabric from hypochlorite bleaching may bleach some dyes and an anti-chlor treatment of the goods, reducing the chlorine with sodium bisulphite, is then useful before dyeing. Corrosion of the steel in dyeing machines by sodium chloride is a constant concern. This is worse at higher dyeing temperatures and then the more expensive Glauber's salt ($Na_2SO_4.10H_2O$) or calcined sodium sulphate (anhydrous) will be preferred. Half the weight of the anhydrous salt is sufficient.

Longer dyeing times and higher temperatures increase the risk of reduction of some azo direct dyes by reducing groups in the cellulose. This is more likely to occur with the lower molecular weight viscose fibres under alkaline conditions. Ammonium sulphate in the dyebath acts as a slightly acidic buffer to prevent this type of reduction. Alternatively, azo dye reduction by the cellulose can be suppressed by addition of a mild oxidising agent such as the sodium salt of *m*-nitrobenzene sulphonic acid. Dyeing with direct dyes is carried out in neutral solution. It is necessary to carefully neutralise the goods after alkaline scouring and bleaching and to know the pH of the water supply. Some direct dyes are not stable at high dyeing temperatures and labile groups, such as amide groups as in CI Direct Red 83, may hydrolyse.

14.3.4 Rates of dyeing with direct dyes and compatibility

The rate of dyeing cotton with direct dyes can vary widely from dye to dye. Times of half dyeing of viscose with direct dyes varied by 2–3 orders of magnitude, when determined for dyeings in which the final exhaustion was limited to 50% by changing the concentration of added salt in each case (Section 11.2). Fortunately, under practical dyeing conditions, giving economic exhaustion, dyeing rates do not vary by more than ten-fold.

Rates of dyeing with single direct dyes are very dependent on the actual dyeing conditions and may not be a good guide to their properties in the typical dye mixtures used in most commercial dyeings. Ideally the dye mixture should behave as a homogeneous dye. As dyeing proceeds, the colour of the goods will gradually become deeper but will then always be of the same hue. For this, the dyes in the mixture must have similar rates of exhaustion and are said to be compatible. The compatibility of direct dyes depends on the rates of dyeing and migration, and the salt sensitivity of the dyes. Hue differences as dyeing proceeds are much more apparent than depth differences. Incompatible dyes also tend to give unlevel dyeings. They have different rates of migration, different degrees of fibre penetration because of dissimilar diffusion rates, and give a change of fabric hue during dyeing because of differences in their overall rates of absorption.

It is preferable to select compatible dye combinations from within each SDC classification group. Combination of some Group A and B, or Group B and C dyes, is possible, however, because of similarities in their properties. Ideally, all the selected dyes should have similar rates of exhaustion and often have the same molecular ionic charge. Dyes with low rates of exhaustion but good migration (SDC Class A dyes) are useful for shading towards the end of the dyeing process.

A dip test is useful for establishing dye compatibility. Small pieces of cotton of equal weight are dyed in the same bath with a mixture of direct dyes. At various intervals, a small dyed sample is removed from the bath and replaced by an identical piece of undyed fabric. A series of dyed samples arranged in order of increasing dyeing time will have gradually decreasing colour depth, but invariant hue, when the dyes used are compatible. When this is so, the series of samples that were added to the dyebath during dyeing will be of increasing colour depth, but also with the same constant hue, when arranged in order of their dyeing times. The results of compatibility tests for direct dyes are only valid under the given dyeing conditions. Rates of exhaustion are very dependent upon the dyeing temperature and salt concentration. For example, for a mixture of CI Direct Blue 1 (**5**, Figure 14.3) and Direct Yellow 12 (**6**) at 60 °C, the yellow dye dyes cotton more rapidly than the blue dye in 0.01 M NaCl, but less rapidly in 0.10 M NaCl.

For some mixtures of two direct dyes, the presence of the second dye reduces

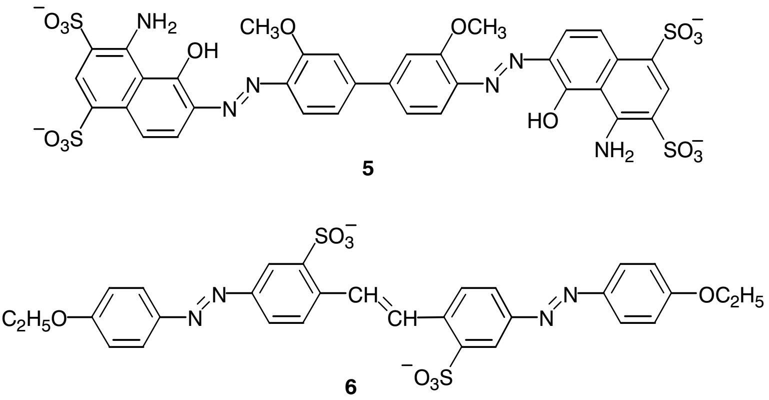


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Figure 14.3 CI Direct Blue 1 (**5**); Direct Yellow 12 (**6**)

the equilibrium exhaustion of the other component. The formation of a complex of the two dyes in the dyebath would explain this. Spectrophotometry of the dye solutions sometimes confirms such complex formation. The spectrum of a solution of the two dyes at room temperature is not the simple sum of the two individual spectra of the separate dye solutions, indicating some interaction between them. Whether this is significant at higher dyeing temperatures is debatable. CI Direct Blue 1 and Yellow 12 show this behaviour and give some unusual dyeing results. For example, the series of dyeings obtained with a mixture of these two dyes, carried out at increasing constant temperatures, becomes paler and bluer. As the dyeing temperature increases, the amount of the yellow dye on the cotton decreases significantly. Surprisingly, the amount of the blue dye increases slightly, contrary to its behaviour when dyed alone at the same temperatures. In dyeing with direct dyes, there are many unexplained phenomena. Obviously, the selection of direct dyes for application in combination requires care, advice from the dye supplier and some preliminary dyeing trials.

14.4 THE EFFECTS OF VARIATIONS IN DYEING CONDITIONS

14.4.1 The influence of added salt

Gradual addition of salt to the dyebath assists direct dye exhaustion onto cellulosic fibres. The actual effects of this on the rate of dyeing vary considerably from dye to dye. The salt provides sodium ions to counteract the negative surface potential of the wet cotton. All fibres immersed in water develop a negative surface potential. This is a characteristic of any two different phases in contact – one will develop a small, electric charge at its surface, opposite in sign to the charge of the other phase. This occurs because one surface is a better electron acceptor than the other. In the case of cellulose at pH 7, water is a better electron donor than the cellulose. Negatively charged carboxylate groups, from oxidation of the primary alcohol group on carbon-6 in some glucose units, also augment the surface charge.

The negative charge of the cellulose surface repels anionic dye molecules. A high concentration of surrounding sodium ions counteracts this. Rapid solution flow also helps to break down the surface layer in which this charge is effective. Direct measurement of the potential difference between the inside of the fibre, where the dye is adsorbed, and the external solution is impossible. Streaming or zeta potentials, which develop when aqueous solutions flow across a fibre plug held between electrodes, can be measured. The values are probably lower than the total potential difference between the inside of the fibre and the external solution. As expected, the negative zeta potential of cotton is reduced by salt solutions, particularly those containing polyvalent metal ions, and increased by adsorption of anionic direct dyes.

The influence of added salt is the most important factor in the dyeing of cellulosic fibres with direct dyes. In dyeing, there are two objectives: good exhaustion and good colour uniformity. Both depend on the salt-controllability of the dyes, or how the gradual salt additions during dyeing influence the rate of exhaustion. Unfortunately salt-controllability is very dependent on the dyeing temperature. For practical purposes, it is useful to have some idea of the degree of exhaustion at different salt concentrations for each dye, possibly at different dyeing temperatures. For two dyes having about the same substantivity, salt should have a greater influence on the exhaustion of the one with the larger number of sulphonate groups, and therefore the larger negative molecular charge. The fibre's negative surface potential repels the more highly charged dye molecules to a greater extent so this dye will respond more to salt additions. This conclusion, however, is not necessarily of great practical value because commercial direct dyes already contain much electrolyte.

The nature of the anion of the added electrolyte has little influence on the amount of adsorbed dye. Therefore, NaCl and Na_2SO_4, at the same total sodium ion concentration, have about the same influence. A higher positive charge on the cation promotes increased adsorption because polyvalent metal ions counteract the negative surface potential more effectively, thus decreasing the repulsion of approaching dye anions. Polyvalent metal salts are, however, much more expensive than sodium chloride, the usual choice of the dyer.

14.4.2 The effect of temperature

Increasing temperature increases the rate of dyeing and of dye migration. From Le Chatelier's principle for an exothermic dyeing equilibrium, the exhaustion will decrease as the dyeing temperature increases, as for some direct dyes on cellulosic fibres ((a) in Figure 14.4). Despite this, higher dyeing temperatures ensure good levelling and better penetration of the dye into the fibres in tightly packed yarns. In practice, such direct dyes are often allowed to finally exhaust in a cooling bath. For isothermal dyeings at increasing temperatures, some dyes, however, show an initial increase in equilibrium exhaustion, up to a temperature of maximum exhaustion, after which the exhaustion then decreases again as the dyeing temperature increases more ((b) in Figure 14.4). Still others, exhibit only increasing exhaustion at temperatures up to the boil ((c) in Figure 14.4).

These diverse variations of direct dye exhaustion depend on two opposing influences of the increasing dyeing temperature. These are the usual effect of

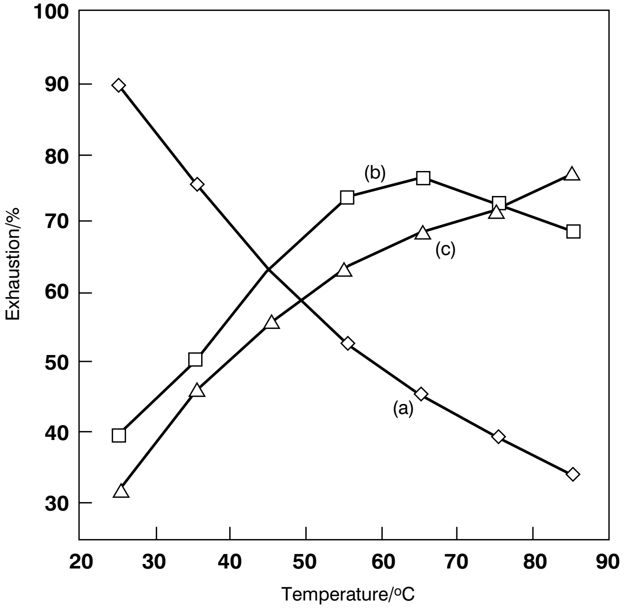


Figure 14.4 Direct dye exhaustion as a function of the dyeing temperature

increasing temperature decreasing the dyebath exhaustion because dyeing is exothermic, and its enhancement of the dyeing rate particularly at lower temperatures. Increasing temperature also promotes dye de-aggregation in the dyeing solution liberating more individual dye molecules to enter the fibre.

Manufacturers often cite a temperature of maximum exhaustion and provide optimum dyeing temperature profiles. The dyes CI Direct Yellow 12, Direct Red 81 and Direct Yellow 28 have maximum exhaustion at 30 °C, 60 °C and 100 °C, respectively, corresponding approximately to the behaviour of dyes (a), (b) and (c) in Figure 14.4. Despite this, the actual dyeing temperature may often depend on machinery limitations. For example, open jig dyeing machines cannot achieve dyeing temperatures much above 85 °C.

14.4.3 The influence of dyeing pH

Dyeing with direct dyes is usually carried out in neutral solution. Under alkaline conditions, cellulose fibres have an even greater negative potential, partly because of increasing dissociation of a number of cellulose hydroxyl groups, and exhaustion is lower. Oxycellulose, present in cotton that has been over-bleached, has a higher proportion of carboxyl groups, and is dyed much paler than undamaged cellulose because carboxylate ions repel the dye anions of like charge. Dyeing in the presence of formic acid suppresses ionisation of the carboxyl groups and the oxycellulose is then dyed to about the same depth of shade as regular cellulose. Under alkaline conditions, reducing end groups, particularly prominent in low molecular weight celluloses such as viscose, reduce some azo direct dyes, decreasing the colour yield. In general, however, if dyeing of cellulosic fibres is in acidic solution, only weak acids are used and the residual acid in the goods is thoroughly rinsed out before drying. Strongly acidic dyeing conditions favour the acid-catalysed hydrolysis of cellulose. Any traces of residual mineral acid dried into the material can cause considerable damage.

14.4.4 The effect of liquor ratio

As we saw in Section 10.4.3, dyebath exhaustion should increase with decrease in the dyeing liquor ratio. This is certainly the case for direct dyes. This means that dyeing at low liquor ratio decreases the amount of waste dye in the effluent. It also consumes less water and steam, and allows a given salt concentration with less added salt. There has been a strong trend towards dyeing at as low a liquor ratio as is practicable. It should always be remembered, however, that the required amount of dye must then be dissolved in a bath of reduced volume. It is important to ensure that the dye is, in fact, in solution at the beginning of dyeing when the temperature is relatively low and after addition of salt.

14.5 THE AFTERTREATMENT OF DYEINGS WITH DIRECT DYES

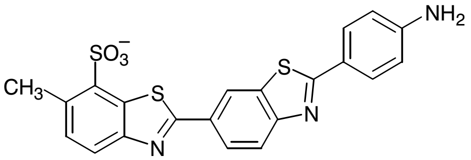
Aftertreatment of dyeings of direct dyes on cellulosic materials aims to improve the washing fastness by increasing the dye's molecular weight. This makes it less soluble and of slower diffusion. Some of these processes decrease the light fastness of the dyeing. Aftertreatments are difficult and costly to carry out, and often give changes in hue that greatly impede shade correction and colour matching. Many of the direct dye aftertreatments now have limited use because reactive dyes give dyeings of much better washing fastness.

14.5.1 Diazotisation and development

Diazotisation of direct dyes with primary aromatic amino groups, followed by coupling of the diazonium ion with an appropriate developer, can be a very effective aftertreatment. Primuline, CI Direct Yellow 59 (**7**, in Figure 14.5), is a classic example of such a dye. Diazotisation involves treating the yellow dyeing with an acidic solution of sodium nitrite at room temperature or lower. Both amine and phenol developers can be used. The diazotised dye in the material is sensitive to light and heat so immediate coupling in a second bath containing the developer is necessary. A final wash removes any dye deposited on the fabric surface to ensure good fastness to washing and rubbing. Although the washing fastness improves by about one grade, there is often a considerable change in hue. For example, a dyeing with Primuline, diazotised and developed with 2-naphthol (**8**), turns from yellow to red. This technique is useful for cheap navies and blacks with a washing fastness of 3–4 but is little used today.

14.5.2 Coupling with diazonium salts

Direct dyes with free positions ortho and para to hydroxyl or amino groups react with an appropriate diazonium ion to introduce one or two additional azo groups. *p*-Nitroaniline, diazotised in a freshly precipitated suspension of its hydrochloride, has been widely used for this purpose.



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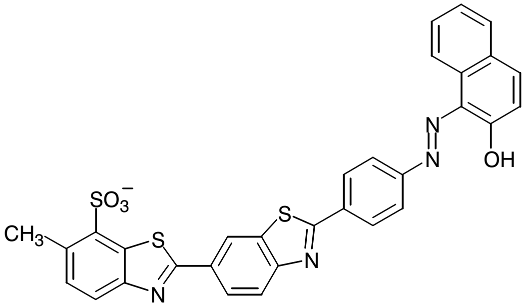

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Figure 14.5 Primuline, CI Direct Yellow 59 (**7**); Primuline diazotised and developed with 2-naphthol (**8**)

14.5.3 Aftertreatment with formaldehyde

This type of aftertreatment is applicable to a few mostly black dyes. Dye molecules are linked by methylene groups, usually in ortho positions to hydroxyl or amino groups. The dyeing is treated with acetic acid and formaldehyde in solution at 70–80 °C. This aftertreatment may result in decreased light fastness.

14.5.4 Metal complex formation

In this type of aftertreatment, cupric or chromic ions convert the dye into a metal complex. The most common ligand structure is a o,o′-dihydroxyazo compound, or its dimethyl ether. In the latter case, the methyl groups are displaced and the dye forms the complex of a dihydroxyazo compound (**9** and **10**, in Figure 14.6). Coppering involves treating the dyeing with acetic acid and copper sulphate solution and heating to 70–80 °C. Complexation usually increases the light fastness. The process results in a change in hue and may be reversible on repeated washing due to de-metallisation. This results in a gradual decrease in washing fastness. Both copper and chromium are environmentally undesirable. Copper aftertreatment is still used for a few brown, navy and black shades, taking care that

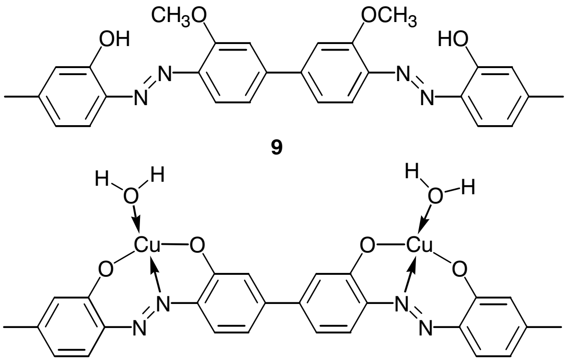

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Figure 14.6

there is a minimum of copper ion in the effluent. Because of this problem, most dye–copper complex dyes are pre-metallised by the dye manufacturers. Even the release in the effluent of the small amounts of copper in unexhausted pre-metallised direct dyes is now reaching the point of exceeding allowable limits.

14.5.5 Cationic fixatives

This aftertreatment involves precipitation of anionic dyes in the cotton with a cationic surfactant or polymer in warm water. It tends to reduce the fastness to light of the dyeing. The change in hue is only slight.

14.5.6 Resin and crosslinking agents

Amino resins and crosslinking agents impart dimensional stability to cotton and viscose fabrics and provide crease resistance and easy care properties. These finishes also improve the wet fastness of direct dyes but again may decrease the light fastness and give a hue change.

The Indosol SF range of dyes (Clariant) are SDC Class B and C copper complex direct dyes. After dyeing, the cotton fabric can be finished by padding with Indosol CR liquid, followed by drying and curing. This imparts dimensional stability and crease recovery as well as good washing fastness and moderate to good light fastness.

14.6 DYEING DIFFERENT TYPES OF CELLULOSIC FIBRES

Cellulosic fibres include cotton, mercerised cotton, linen and the various forms of viscose, each with their own particular dyeing characteristics. Because of the differences in molecular weight and morphology between native and regenerated cellulose fibres, there are large differences in their physical properties. Wet cotton is a strong, rigid fibre and most woven cotton fabrics will withstand considerable stress. This is not true of fabrics made from regular viscose. Their wet strength is only moderate and they require careful handling during dyeing. Viscose also swells much more than cotton when wetted. This can lead to limited solution flow and dye penetration problems in dyeing packages or packed loose fibre.

The different types of cellulosic fibre are all dyed by direct dyes using essentially the same dyeing method. The temperature increase of the dyebath, and the amount of salt added to it, control the rate of exhaustion and levelling. In the dyeing of blends of these cellulose fibres with direct dyes, they do not absorb dyes at the same rate or to the same extent because of the differences in their morphology. Even the extent and conditions of drying after preparation can influence the dyeing of a fabric of cellulosic fibres. Despite these differences, the standard affinity of a given direct dye is remarkably constant for the different cellulose fibres.

The effects of carboxylate groups are important at low salt concentrations where there is little effective shielding of their negative charge by sodium ions. The higher negative surface charge of viscose compared with cotton is partly because of its additional carboxylate groups. In general, with more than 2 g l^{-1} NaCl, the extent of dye absorption increases in the order cotton, mercerised cotton, regular viscose; in the same order as increasing fibre accessibility. Even different grades of cotton fibre have different dye absorption characteristics. This is one reason why intimate blending of cotton fibres before spinning is so important.

The rate of dyeing increases as the diameter of a fibre decreases, even though the equilibrium exhaustions for chemically identical fibres with different diameters hardly vary. This is readily demonstrated for viscose filaments of different denier. The internal volume of the pores is different for the various cellulosic fibres. These internal volumes have been estimated to be 0.30, 0.50 and 0.45 l kg^{-1} for cotton, mercerised cotton and regular viscose. A value of 0.22 l kg^{-1} is widely used for cotton in estimating dye affinities (Section 11.1.2). In dyeing, these fibres are far from being saturated with dye, so the dye only adsorbs onto a very small part of the internal surface.

Covering neps of immature cotton fibres (Section 5.2.3) is always a concern in cotton dyeing. With dyes of low substantivity, neps usually absorb less dye and appear as paler spots on the fabric. Since immature fibres give much greater rates of dye desorption, the paler dyed neps may not appear until after washing. Better coverage can be achieved using dyes of high substantivity and can be much improved by mercerisation before dyeing, since this swells the immature fibres (Section 5.4.6).

Mercerised cotton will absorb more dye and be darker in colour than normal cotton dyed in the same bath. It is more accessible than regular cotton and its lower negative surface potential decreases repulsion of dye anions. It will appear darker in colour even for the same amount of dye in the fibre because of a higher degree of internal light scattering that results in greater light absorption. This effect is, however, dependent on the dye being used and the conditions of mercerisation.

Viscose fibres and filaments are available in a number of variants with different dyeing characteristics. They have different internal structures, skin-to-core ratios, porosities and degrees of fibrillation. These different forms therefore have different dyeing rates, equilibrium dye absorptions and colour yields. Direct dyes have higher substantivity for regular viscose than for cotton because viscose is less crystalline and oriented so it has a much greater internal surface. The fastness to light of dyeings of direct dyes on viscose is up to one fastness grade better than on cotton. The fastness to washing on viscose, however, is often less than on cotton because of its higher accessibility. The more highly oriented viscose types give better wet fastness.

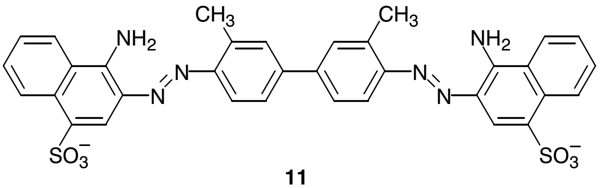
The physical and chemical properties and the dyeing behaviour of the various cellulosic fibres are therefore quite different. About all they have in common, is the cellulose that constitutes them.

14.7 THE ORIGINS OF SUBSTANTIVITY FOR CELLULOSE

The dyeing of cotton with direct dyes is completely reversible. For dyeings at equilibrium, the Freundlich isotherm usually applies (Section 11.1.1) but some dyeings with direct dyes give a better correlation with the Langmuir isotherm. The former isotherm usually indicates that adsorption is non-specific and the latter that the dye adsorbs on specific fibre sites. This dichotomy of behaviour is typical of the poor understanding of dyeing cellulose fibres.

Direct dyes invariably have extended, conjugated, coplanar molecules, with widely spaced hydrogen bonding groups and some sulphonate groups to provide solubility in water. The greater the number of sulphonate groups in the dye molecule, the higher the water solubility but the lower the fastness to wet treatments, and the lower the dye substantivity. Molecular coplanarity is, however, a specific requirement for substantivity. Whereas the dye Benzopurpurine 4B (**11**, in Figure 14.7) has good substantivity for cotton, its isomer meta-Benzopurpurine (**12**), which cannot be coplanar, does not. While most dyes substantive to cellulose fibres are coplanar, they are not always long and linear (see Chapter 17 on vat dyes).

Long, coplanar dye molecules can sit on top of a cellulose polymer chain with the aromatic rings parallel to the glucose rings. This would allow short range intermolecular attractive forces to operate. This interaction has long been considered to involve hydrogen bonding. Cellulose has an abundance of hydroxyl groups and direct cotton dyes often have hydroxyl, amino or amide groups capable of hydrogen bonding. This interpretation of the origin of the substantivity of direct dyes is prevalent in the dyeing literature. It is by no means proven. The cellulose hydroxyl groups are in the equatorial positions around the glucose units and do



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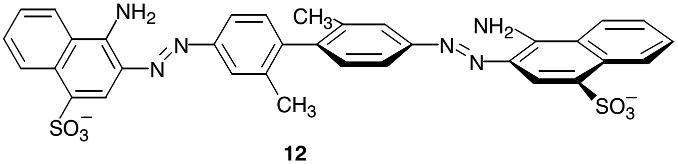

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Figure 14.7 Benzopurpurine 4B (**11**); meta-Benzopurpurine (**12**) not necessarily present an appropriate angle to the hydrogen bonding groups in the dye molecule when the latter is sitting above or below the glucose ring. Cellulose hydroxyl groups are usually hydrogen bonded together or to water during dyeing. Many leuco vat dyes, derived from polycyclic quinones and leuco sulphur dyes (Chapter 17) have high substantivity for cellulose fibres, yet they have neither linear structures nor many hydrogen bonding groups. Substantivity may therefore depend more on van der Waals and dispersion forces between the dye and fibre molecules.

Substantivity may also involve the surface active properties of direct dyes. The more hydrophobic sections of the dye molecule would prefer to approach the relatively hydrophobic axially oriented carbon–hydrogen bonds of the glucose rings in cellulose to avoid interaction with surrounding water molecules. This is the driving force of surface activity. Since cellulosic fibres are extremely porous, they have an extended internal surface and surface activity effects could account for a considerable degree of dye adsorption.

Direct dyes aggregate in solution and in the fibre, another facet of their surface activity. There is circumstantial evidence that aggregation of the dye molecules in the cellulose fibre is the cause of the dye's substantivity. Dye aggregation increases with increasing dye and salt concentration, and decreases with increasing temperature. Most evidence suggests that aggregation is not significant in boiling solutions but the inability of the limited experimental techniques to detect small aggregates in solution, or in the fibre, could give misleading conclusions. Some dyes do not appear to aggregate, but are substantive (CI Direct Yellow 12). Others are so highly aggregated that dyeing is almost impossible at low temperatures (copper phthalocyanine direct dyes), and others appear to have no substantivity unless salt is present (CI Direct Blue 1).

Despite the considerable literature on the effects of varying molecular structure on the substantivity of dyes for cotton, the origins of such substantivity are poorly understood. Are both dye–fibre and dye–dye interactions as well as surface activity involved in promoting substantivity of direct dyes for cellulosic fibres? The best answer one can give is – possibly. How little we understand of this technology.

REFERENCES

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CHAPTER 15

Disperse dyes

15.1 INTRODUCTION TO DISPERSE DYES

Cotton can be dyed with anionic direct, sulphur, vat, reactive and azoic dyes. These types of dyes, however, are of little use for the dyeing of synthetic fibres. Disperse dyes, on the other hand, are non-ionic. They dye all the synthetic and cellulose acetate fibres using a direct dyeing technique. Only the dyeing temperature varies from one fibre to another. They are thus one of the major classes of dyestuff. The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough. Their major use today is for the coloration of polyesters, the most important group of synthetic fibres.

What is a disperse dye? These non-ionic dyes are relatively insoluble in water at room temperature and have only limited solubility at higher temperatures. They do, however, possess substantivity for hydrophobic fibres such as nylon and polyester, in which they are quite soluble. As their name implies, these dyes are present in the dyebath as a fine aqueous suspension in the presence of a dispersing agent. The water dissolves a small amount of the dye in monomolecular form. The hydrophobic fibres then absorb the dye from the solution. Because these dyes are non-ionic organic compounds of relatively low molecular weight, many sublime on heating and dyeing by absorption of the dye vapour is also possible.

When cellulose diacetate fibres first appeared in 1921, few of the available ionic dyes were able to successfully colour them. Secondary acetate fibres absorb little water, do not swell and have only small pores. In addition, their surface potential is much more negative than that of cotton and therefore they repel anionic dyes. Although cellulose diacetate fibres will absorb some cationic dyes, and a few acid dyes, there is little or no penetration of the dye unless the fibre is pre-swollen. The dyeings produced using ionic dyes also have poor fastness properties.

The first dyes for cellulose acetate fibres were water-soluble. The dye molecules

$$\text{Dye—NH—CH}_2\text{SO}_3\text{Na(aq)} + \text{H}_2\text{O} \longrightarrow \text{Dye—NH}_2\text{(s)} + \text{CH}_2\text{O(aq)} + \text{NaHSO}_3\text{(aq)}$$

Scheme 15.1

contained a methylamino sulphonate group (–$NHCH_2SO_3Na$) introduced by reaction of a primary amino group with formaldehyde and sodium bisulphite (Ionamine dyes, 1922). During dyeing, this group hydrolysed to the less soluble parent amine (Scheme 15.1). It was soon recognised that it was this compound that the cellulose acetate absorbed. The first true disperse dyes were simple, relatively insoluble azo and anthraquinone compounds dispersed in water using the sodium salt of sulphated ricinoleic acid (**1**, in Figure 15.2). Many of these dyes are obsolete but their development provided the technology for preparing fine aqueous dispersions by grinding the dye with dispersing agents. A fine dispersion is essential for rapid dyeing and avoids deposition of larger dye particles on the material.

Disperse dyes have slight water solubility because of the presence of polar substituents in their molecular structures. During dyeing, a small quantity of dye is present in true aqueous solution in a monomolecular form. These dye molecules are able to penetrate into hydrophobic artificially-made fibres such as those of cellulose acetate, nylon or polyester. The dye is much more soluble in the fibre than in water so deep dyeings are possible. The dye particles in dispersion are very small. Their large specific surface area ensures rapid solution to maintain saturation of the aqueous solution as the soluble dye transfers to the fibre. Dyeing consists of a solubility equilibrium coupled to a solid solvent extraction equilibrium (Scheme 15.2).

$$\text{Dye(s)} \rightleftharpoons \text{Dye(aq)} \rightleftharpoons \text{Dye(fibre)}$$

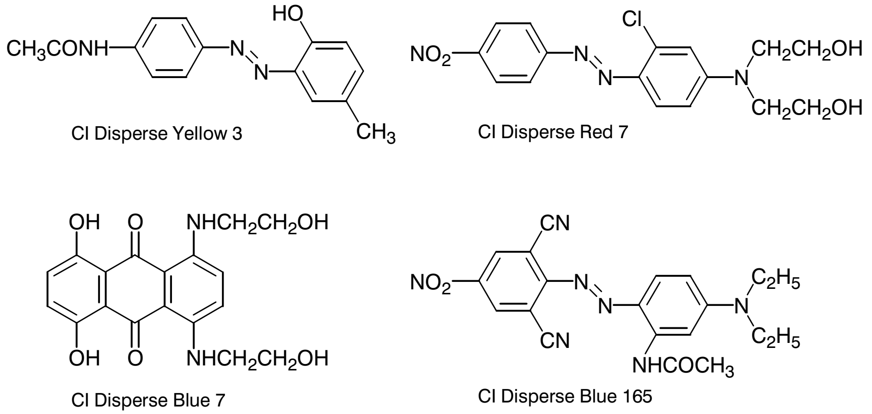
Scheme 15.2

Dyeing isotherms, graphs of C_f (concentration of dye in the fibre) as a function of C_s (concentration of dye in solution) at a given constant temperature, are of the linear Nernst type (Figure 11.1). This is true whether the equilibrium is established starting with undyed fibres and an aqueous dispersion of the dye, or with the dyed fibre and water. The final point on the linear portion of the isotherm gives the solubilities of the dye in the fibre and in water. Beyond this point, the dye saturated fibre is in equilibrium with the saturated aqueous solution, which is in equilibrium with solid dye particles. The slope of the isotherm gives the value of the partition coefficient (C_f/C_s). This dyeing equilibrium constant decreases with increasing temperature since dyeing is exothermic.

15.2 CHEMICAL CONSTITUTIONS OF DISPERSE DYES

The majority of disperse dyes are low molecular weight, non-ionic mono-azo and anthraquinone derivatives. Polar substituents are usually present in the dye molecule so that the dye has the slight solubility in water required for dyeing. Hydroxyethylamino groups ($NHCH_2CH_2OH$) are typical of such substituents. The interaction of such polar groups with the water, by dipole interactions and hydrogen bonds, is crucial for water solubility. Dipole forces and hydrogen bonds, as well as dispersion forces, also bind the dye molecules to polar groups in the fibres.

There are many thousands of azo disperse dye structures because of the numerous substitution patterns possible in the diverse diazonium ion and coupling components. Colours that are less typical of simple azo compounds, such as greenish-yellow and blue, are also possible using more specialised components. These may have heterocyclic units or cyano substituents. There is also a limited number of other chromophores providing disperse dyes with particular properties. Figure 15.1 gives some typical disperse dye structures.



CI Disperse Yellow 3

CI Disperse Red 7

CI Disperse Blue 7

CI Disperse Blue 165

Figure 15.1 Some typical disperse dye structures

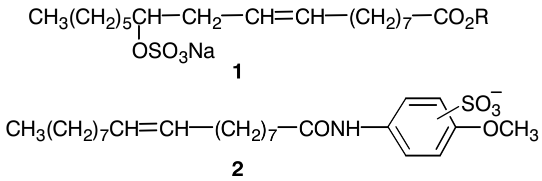
Anthraquinone disperse dyes are usually 1-hydroxy or 1-amino derivatives. These have bright colours ranging from red through to blue. Simple anthraquinone dyes have low molar absorptivities (Section 24.1) compared to azo compounds and therefore give dyeings of lower colour yield. Apart from a few bright pinks and blues, anthraquinone disperse dyes are gradually being replaced. In their manufacture, the production of the required intermediate chemicals, and of the dyes themselves, often involves complex reactions under pressure. The reaction equipment is more sophisticated than that used for the simpler azo coupling reaction. In addition, anthraquinone-1-sulphonic acids are key intermediates and the sulphonation reactions for their preparation use a mercuric ion catalyst. The environmental threat of mercury in the chemical plant effluent has led to increasingly stringent regulations for its containment and therefore increased production costs.

There are no true green or black disperse dyes. Dyes with both red and blue light absorption bands for greens, or with several overlapping absorption bands for blacks, are difficult to prepare. A major constraint for disperse dye structures is the relatively low molecular weight that the dye must have to be slightly water-soluble and to be able penetrate into hydrophobic synthetic fibres. A combination of blue and yellow dyes gives green dyeings. Blacks require an aftertreatment of the dyeing involving diazotisation of the absorbed dye containing a free primary amino group followed by reaction with a coupling component. Black disperse dyes may also be mixtures of dull orange, rubine and navy dyes. Many disperse dyes are mixtures generated by the reactions used in their synthesis. Techniques such as thin layer chromatography are useful for establishing the number of components (Section 24.5.3).

15.3 DISPERSE DYE DISPERSIONS

Disperse dyes are available as powders, grains, pastes or aqueous dispersions. These all contain micro-fine dye particles, many with diameters below 1 μm, as well as varying amounts of dispersing agents. Powders may cause dusting but this is not as bad as with some ionic dye powders. Granular forms pour easily, dust less and facilitate weighing. Solid forms of the dyes contain much more dispersant than pastes and liquid forms to prevent particle aggregation during drying. Liquid disperse dyes are useful for continuous dyeing. Settling and aggregation of dye particles in pastes and liquids can lead to coloured specks on the dyed fabric. Powdered or granular disperse dyes rarely contain more than 50% dye, the rest being dispersant plus smaller amounts of diluents, oils and shading colours.

The role of the dispersing agent is to coat the surface of each dye particle with a monomolecular layer of adsorbed dispersant. Since these chemicals are invariably anionic polymers, the more hydrophobic sections of the polymer chain adsorb onto



$CH_3(CH_2)_5\underset{OSO_3Na}{CH}—CH_2—CH=CH—(CH_2)_7—CO_2R$

Figure 15.2 The original disperse dye dispersing agent, sulphated ricinoleic acid (**1**); a modern dispersant, sodium oleyl-*p*-anisidide sulphonate (**2**)

the hydrophobic dye particle surface with the anionic groups of the polymer exposed to the surrounding water. The overall negative charge on the surface of each particle prevents their coalescence and aggregation. The original dispersant was sulphated ricinoleic acid (1, in Figure 15.2). Modern dispersants are often either lignosulphonates from paper pulping, sulphonates of alkylnaphthalene-formaldehyde condensates (Figure 15.3), or sodium oleyl-*p*-anisidide sulphonate (2). Many commercial dispersants for dyeing are mixtures of non-ionic and anionic compounds. The dye particles dissolve in the micelles of the non-ionic surfactant and the anionic component raises the cloud point of the former (Section 9.3.3) to values above the dyeing temperature so that the dispersion is stable.

The presence of a dispersing agent in the dyebath increases the apparent water solubility of the dye and therefore decreases the dyeing exhaustion. This is because dispersant micelles in solution dissolve an appreciable number of dye molecules. The number of dye molecules per solid particle is much larger than the number per surfactant micelle. The number present as single soluble molecules in true solution is even less. All these dye species appear to be in rapid equilibrium in the dyebath. Therefore, dye transferred from the aqueous solution to the fibre is rapidly replenished by dye from a micelle or from a particle surface.

To ensure that the rate of solution of the dye does not control the overall rate of dyeing, the dyes consist of very small particles to give the maximum specific surface area. Therefore, during dyeing the average particle size will gradually increase because the smaller particles dissolve more rapidly. The very fine state of division avoids dye specks on the goods. In fact, the quality of the fine dispersion is often evaluated by running it through coarse filter paper and examining for any coloured residue. Dispersions may not always be stable under the dyeing conditions, particularly those involving high temperatures and high shear forces as

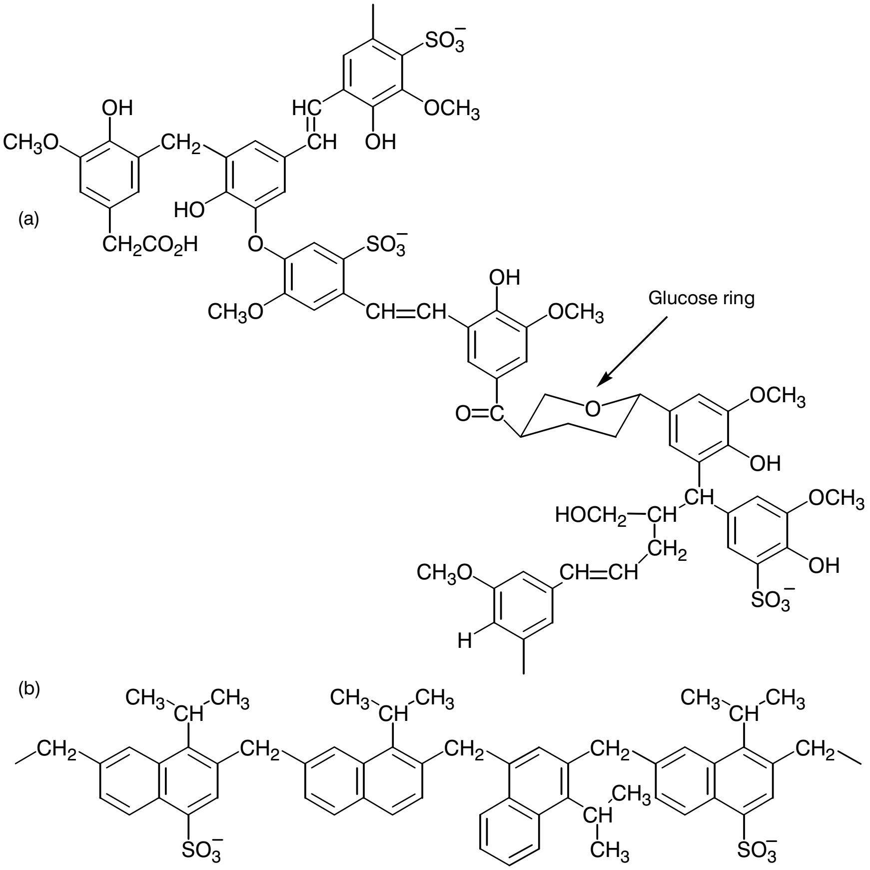


Figure 15.3 Partial chemical structures of lignosulphonate (a) and alkylnaphthalene sulphonate – formaldehyde condensate (b) dispersing agents

in jet and package machines. The dyebath usually contains additional dispersant to maintain the dispersion of the dye and to promote levelling. This is more important for pale shades when the amount of dispersant added from the dye powder or liquid is low. No electrolyte is added to the dyebath since it will not influence the dyebath exhaustion. Disperse dyes are non-ionic and the negative water–fibre boundary charge does not influence adsorption. Salt addition often affects the layer of anionic dispersant on the surface of the dye particles, resulting in undesirable particle aggregation.

As always in dyeing, good quality water is essential. Some dyes react with traces of metal ions such as iron or copper and give shade changes. Calcium and magnesium ions may react with anionic dispersants and wetting agents rendering them much less effective. Addition of a sequestering agent is valuable, especially with metal-sensitive dyes.

15.4 FASTNESS PROPERTIES OF DISPERSE DYES

The fastness to washing and light of dyeings with disperse dyes on synthetic and acetate fibres is usually moderate to good (Table 15.1). The washing fastness on nylon, however, is only fair, particularly for deep shades. The results of washing fastness tests on deep polyester dyeings often depend upon how well residual disperse dye particles on the fibre surface have been cleared after dyeing. When disperse dyes have migrated from inside the polyester fibre to the surface during thermal treatments such as heat setting or drying, the dyeings may have reduced fastness to washing, dry cleaning and rubbing (crocking). This effect is enhanced when the dyes are soluble in hydrophobic surface finishes such as softeners. The fastness to wet treatments of dyeings on secondary cellulose diacetate is inferior to that on the more hydrophobic triacetate. The summary in Table 15.1 shows that dyeings of artificially-made fibres with disperse dyes generally have good fastness properties. For any fibre, however, a particular fastness property will vary considerably from dye to dye.

Table 15.1 Typical fastness properties of disperse dyes on all synthetic fibres

Fastness property	Acetate	Triacetate	Nylon	Polyester	Acrylic
Washing	Moderate	Good	Poor to fair	Good	Very good
Light	Good	Good	Moderate to good	Good	Good
Crocking	Good	Good	Good	Moderate to good	Moderate
Gas fume fading	Fair	Moderate	Fair	Moderate	Good

The light fastness of disperse dyes may be very good in standard shades but is less so for pale shades, and lower still for tests conducted using a carbon arc light source. Non-ionic UV absorbers increase the light fastness for dyed fabrics such as those used for automobile upholstery.

Certain blue and violet anthraquinone disperse dyes with basic amino groups are very sensitive to fading by nitrogen dioxide in polluted air. High temperature combustion processes produce low concentrations of nitrogen oxides. They are most abundant in industrial or city environments. Their effect on dyeings is called gas fume fading. This type of fading is usually worst for dyeings with sensitive dyes on cellulose acetate fibres. It is less severe on nylon and polyester fibres, but still poses a problem when the highest fastness is required. Nitrogen dioxide will nitrosate a relatively nucleophilic primary amino group of the dye, converting it into a hydroxyl group. This reaction usually reddens the shade. Colourless fading inhibitors protect sensitive dyes. These are readily nitrosated amines that preferentially react with the nitrogen dioxide and thus protect the dye. The fading inhibitor is added to the dyebath towards the end of dyeing, or is applied in an aftertreatment. Dyes that are more resistant to nitrogen dioxide fading have less nucleophilic phenylamino groups.

Ozone is a major air pollutant in metropolitan centres. It causes oxidation of many types of dyes, close to the fibre surface. Ozone fading of dyed nylon carpets and fabrics in automobile interiors is particularly serious for pale shades when the dye has not adequately penetrated into the fibres (Section 13.12). Aftertreatment of the dyeing with amine or phenol anti-oxidants, similar to gas fume fading inhibitors, improves the fastness to ozone fading of sensitive blue anthraquinone disperse dyes [1].

15.5 DYEING CELLULOSE ACETATE FIBRES

The dyeing of cellulose acetate materials is a simple direct dyeing process. The dispersion of dyes in warm water is sieved into the bath, possibly already containing additional dispersant. Boiling water and concentrated solutions of dispersing agents must be avoided as they can adversely affect the dye particle dispersion. Cellulose diacetate is dyed at temperatures not exceeding 85 °C, because of the risk of acetyl group hydrolysis on the fibre surface, which causes considerable dulling of the attractive lustre of the bright filaments. Because this thermoplastic material readily forms permanent creases at the usual dyeing temperature of 80–85 °C, dyeing of the full width fabric on a roller is necessary. A typical jig dyeing procedure involves two ends at 40–50 °C, followed by two ends at each higher bath temperature, up to the final dyeing temperature of 80–85 °C. At the higher temperatures, the lengthways tension must be as low as possible, to avoid elongation of the fabric. Beam dyeing is possible provided that the material allows good liquor flow through the roll at a pressure low enough to avoid deforming the plastic filaments

Disperse dyes for cellulose acetate vary widely in their rates of exhaustion and levelling ability. Dyeing with mixtures of compatible dyes is essential. The SDC gives testing procedures for dyeing cellulose diacetate with disperse dyes [2]. These tests establish the migration ability of the dye, the influence of temperature on dye uptake (temperature range test), the rate of dyeing and the colour build-up with increasing dye concentration relative to standard dyes of known properties.

The results of the temperature range test provide classic examples of the influence of temperature on dyeing kinetics and equilibrium. For dyes that adsorb rapidly at 50–60 °C, the amount of dye absorbed after dyeing for an hour will decrease as the dyeing temperature increases. This is the expected effect of temperature on an exothermic dyeing process that has reached or come close to equilibrium. The exhaustion (equilibrium constant) decreases with increasing temperature. For slow dyeing dyes, the amount of dye absorbed in one hour increases steadily with increasing dyeing temperature because this increases the rate of diffusion of dye into the fibre. After dyeing for one hour, the dyeing may be sufficiently far from equilibrium that the expected decrease of the exhaustion with increasing temperature does not occur. Some dyes may show a temperature of maximum dye exhaustion, showing the effects of temperature on dyeing rate at lower temperatures and on exhaustion at higher values. Slow dyeing dyes with poor temperature range properties will likely cause ending and listing when dyeing on a jig (Section 12.4.2) because the fabric ends and selvages tend to be cooler than the bulk of the material.

Blacks can be obtained in one of two ways. The simplest involves the use of a mixture of dull red, blue and yellow or orange disperse dyes at relatively high total concentrations. With appropriate combinations, this is quite successful. The second method is by a diazotisation and coupling aftertreatment. This involves diazotisation of a primary aromatic amino group in the disperse dye in the fibre and subsequent reaction of the diazonium ion with a suitable coupling component such as 3-hydroxy-2-naphthoic acid (BON acid after beta-oxy-naphthoic acid). Coupling in alkaline solution, as in the aftertreatment of direct dyes on cotton (Section 14.5.1), is less suitable for cellulose acetate because of the risk of surface hydrolysis of acetate groups. The amino disperse dye, for example CI Disperse Black 1 (**3**, in Figure 15.4), is applied by conventional dyeing at 80 °C. After rinsing the orange fabric, the amino groups of the dye in the cellulose acetate are diazotised by reaction with a solution of sodium nitrite and hydrochloric acid at room temperature. After rinsing again, the fabric is treated with a dispersion of BON acid. This is prepared by precipitation of the free acid from a solution of its sodium salt in the presence of a dispersing agent. It is absorbed by the fibres at pH 4.5 exactly like a disperse dye. It reacts with the diazonium ion to form the dark navy pigment (4).

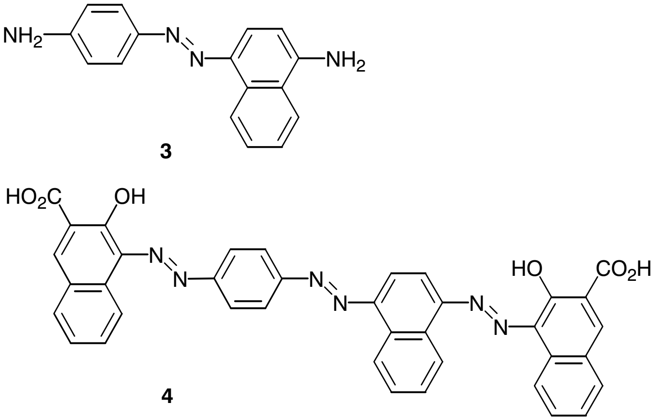


Figure 15.4 CI Disperse Black 1 (**3**); dark navy pigment formed after the disperse dye is diazotised and then treated with a dispersion of BON acid (**4**)

Other sequences for dye application, diazotisation and coupling, are possible. The coupling component can be applied to the fibre after dyeing, as above, or even concurrently along with the amino disperse dye followed by its diazotisation. Once the colour has fully developed, scouring the material in soap or detergent solution at relatively low temperature removes pigment from the fibre surface and biproducts from the diazotisation and coupling sequence. If this is not done, inferior fastness properties result, particularly poor fastness to washing and rubbing.

Cellulose diacetate fabrics must be handled and dyed with care to avoid forming crease marks and stretching. Even at a dyeing temperature of 85 °C, the material is quite plastic and easily deformed. It is therefore preferable to dye such fabrics in open width using a jig machine. This is, however, not as simple as it might seem. Section 12.4.2 outlines some of the problems inherent in jig dyeing. With many disperse dyes, ending and listing effects are all too common, and are particularly noticeable when using less compatible combinations of dyes.

Cellulose triacetate is considerably more hydrophobic than diacetate and dyeing it with disperse dyes requires higher temperatures, but carries less risk of surface hydrolysis. The more compact internal structure gives lower dye diffusion rates in this fibre. It is normally dyed with disperse dyes at the boil. Dyeing temperatures up to 130 °C are possible and give improved washing and crocking fastness because of the better penetration of the dyes into the fibres. This is beneficial when dyeing heavy shades. It also allows use of dyes that are absorbed too slowly at 100 °C, thus increasing the range of available dyes. For dyeing deep shades, dyeing at the boil using a carrier such as diethyl phthalate is possible. This acts as a fibre swelling agent and thus accelerates dye absorption by increasing the diffusion rate (Section 15.7.3). For a typical black, the amino disperse dye and coupling component are applied sequentially, or simultaneously. The black is developed by aftertreatment with a solution of sodium nitrite and hydrochloric acid that causes diazotisation of the dye and immediate coupling of the generated diazonium ion. Soaping removes surface colour, but usually a process called reduction clearing is preferred. In this, the dyed material is treated with a weakly alkaline solution of sodium hydrosulphite (hydros, $Na_2S_2O_4.2H_2O$), which reduces and eliminates the azo pigment on the fibre surface. Each combination of dye and coupling component requires its own particular dyeing and aftertreatment conditions so the dye supplier's recommendations should be consulted.

As for nylon, dry heat setting of cellulose triacetate fabrics improves their dimensional stability but reduces the dyeing rate. If heat setting or texturising has not been uniform, barré effects may be evident on fabrics made of filament yarns. Dyeing under pressure at above 100 °C increases the rate of dye migration and minimises barré effects. For heat pleating of cellulose triacetate materials after dyeing, it is essential to use disperse dyes that do not readily sublime from the heated fibre.

15.6 DYEING NYLON WITH DISPERSE DYES

The use of acid dyes on nylon to produce dyeings of good washing fastness invariably involves the risk of barré because dyes of poor migration do not evenly dye filaments with chemical and physical variations. This risk is almost absent when using disperse dyes. The consequence of their good migration during dyeing, however, is poor to moderate wet fastness, especially in heavy shades. The dyeing of nylon with disperse dyes is therefore limited mainly to pale shades for lingerie fabrics and sheer hose that do not require repeated or severe washing. Disperse dyes on nylon are also more sensitive to fading by ozone and nitrogen dioxide. They are, however, economical and easy to apply.

Most nylon filaments are oriented by drawing but both undrawn and partially oriented yarns can be dyed with disperse dyes. With increasing draw ratio, the increased polymer chain orientation decreases the rate of dyeing (decreased fibre accessibility) but not the extent of dye absorption at equilibrium (unchanged fibre availability). It is only at the very high draw ratios typical of strong industrial yarns that the equilibrium dye absorption decreases. Uniform drawing of filaments is essential. Accessibility differences in dyeing can be minimised provided that the selected dyes and conditions are conducive to levelling. Disperse dyes on nylon are much better in this respect than acid dyes.

15.6.1 Preparation of nylon for dyeing

The preparation of nylon goods for dyeing usually involves scouring with a detergent and soda ash (sodium carbonate) solution at 70 °C. This removes any soluble sizing material, lubricants, and spin finishes that might hinder access of the dye solution to the fibre surface.

Heat setting of nylon fabrics has already been discussed (Section 13.9.3). This process may be performed before or after dyeing, preferably the latter. It causes variations in dye substantivity and may be non-uniform, leading to unlevel dyeings. Dry heat setting in hot air decreases the rate of dyeing of nylon 6.6 and 6 with both acid and disperse dyes, but setting in steam increases their dyeing rates. Steam setting, however, decreases the wet fastness of dyeings with disperse dyes, particularly if setting is carried out after dyeing. The more open fibre structure resulting from heat setting in steam allows easier dye desorption during washing of the dyed material. If it is necessary to bleach nylon that has become yellow from over-vigorous heat setting in dry air, peracetic acid or sodium chlorite solution can be used.

15.6.2 Application of disperse dyes to nylon

The disperse dye is pasted in warm water and the dispersion slowly diluted. Hot water and concentrated dispersant favour the formation of large dye particles. The concentrated dispersion is then strained into the dyebath that usually also contains additional dispersing agent. The bath is gradually heated and dyeing continued at the boil. The disperse dyes used for nylon are usually level dyeing.

The exhaustion rates of individual disperse dyes on nylon are not overly high. They do vary from dye to dye so that selection of compatible dyes is necessary.

Although some dyes have good migration and build up well, deep shades are rarely dyed with disperse dyes because of their inferior washing fastness. Many of the simple disperse dyes developed for dyeing acetate at 85 °C are not particularly fast to heat and can sublime from the nylon during processes such as boarding. This is a form of heat setting used to stabilise the shape of ladies' hosiery after dyeing. Dyes of higher fastness to sublimation are invariably of greater molecular size and therefore have lower rates of dyeing. The usual temperature for rapid dyeing disperse dyes on nylon is 85–100 °C. If slow dyeing heat fast dyes are used, dyeing under pressure at up to 120 °C may be useful. The disperse dyes used for dyeing nylon will also colour spandex (segmented polyurethane) filaments in stretch hose but the washing fastness is only fair. As for cellulose acetates, blacks are produced by diazotisation of a disperse dye containing a primary amino group and coupling of the generated diazonium ion with a suitable coupling component.

Simple dyeing tests evaluate the migration, temperature range characteristics and dyeing rates of disperse dyes on nylon [3]. With rapid dyeing dyes, the dyeing rate increases with increasing temperature but the equilibrium exhaustion decreases. The more rapid dyeing dyes also migrate better and tend to be less temperature sensitive so that dyeings at different temperatures are close in shade.

Nylon 6 is more amorphous and has a lower melting point than nylon 6.6. Disperse dyes dye nylon 6 using the same method as for nylon 6.6. Dyeing is usually faster than for nylon 6.6 under the same conditions and the dyes will usually show better migration. This usually means that the washing fastness is somewhat lower on nylon 6. One advantage of nylon 6 is that heat setting using hot air or steam is at lower temperatures than for nylon 6.6.

15.7 DYEING POLYESTER WITH DISPERSE DYES

15.7.1 The problem of dyeing polyester

Polyester fibres are essentially undyeable below 70–80 °C, leaving only a 20–30 °C range for increasing the dyeing rate before reaching the boiling temperature. At any temperature, the rate of dyeing of polyester with a given disperse dye is very much lower than for cellulose acetate or nylon fibres. The rate of diffusion of disperse dyes into the polyester below 100 °C is so low that dyeing at the boil does not give reasonable exhaustion. The rate of dyeing is higher for dyes of small molecular size that have higher diffusion coefficients. Dyeing is faster when using fibre swelling agents called carriers to improve the fibre accessibility, or when dyeing at higher temperatures above 100 °C to increase the dye diffusion rate.

Fibres of the most common polyester, polyethylene terephthalate (PET or PES), are quite crystalline and very hydrophobic. Hot water does not swell them and large dye molecules do not easily penetrate into the fibre interior. Polyesters have no ionic groups and are dyed almost exclusively with disperse dyes. The better diffusion at the boil of low molecular weight dyes results in moderate migration during dyeing but then the washing fastness is only fair. Many of the more recent disperse dyes are specifically for dyeing polyester. These are of higher molecular weight to provide adequate fastness to sublimation during heat treatments. Some of these produce a reasonable depth of shade by dyeing at the boil. Most, however, require higher dyeing temperatures or carriers for satisfactory results. Dyeings of polyester with disperse dyes have good light fastness. This does not always correlate with the light fastness on other fibres such as cellulose diacetate.

The disperse dyes provide a full range of colours with adequate to good build-up on PET fibres. Uneven filament texturising or heat setting can lead to barré but higher dyeing temperatures, or addition of some carrier, will promote migration to minimise this. Again, a full black requires aftertreatment of the dyeing by diazotisation of an amino disperse dye and coupling with a suitable component, often BON acid. Concurrent dyeing with a mixture of the amino disperse dye and dispersed BON acid, followed by treatment with sodium nitrite and hydrochloric acid, is a common procedure. Some blacks are mixtures of dull yellow, red and blue dyes.

15.7.2 Preparation for batch dyeing of polyester

Loose PET fibre is usually dyed directly without pretreatment because emulsification of the small amount of superficial processing chemicals is easy. This is not the case for knitted goods, that may contain additional oil or wax, or for woven goods with sized warp yarns. Typical preparation involves scouring with 2 g l^{-1} each of soda ash (sodium carbonate) and an anionic detergent at 50 °C. Addition of an organic solvent may be useful if wax or much knitting oil is present. Because the dispersants present in the dyes or added to the dyebath are usually anionic, removal of any cationic auxiliary chemicals in the spin finish is necessary before dyeing.

When fabrics of PET are heated in water at the boil there is often considerable shrinkage as the tensions in the filaments relax. The shrinkage may be even greater at higher temperatures. Fabrics of PET can be dry heat set at 200–225 °C for 30–60 s. Alternatively, steam heat setting at 130–140 °C for several minutes is also possible but can cause a loss of strength due to some hydrolysis of the polyester. Steam setting provides dimensional stability in boiling water but, for stability to ironing, higher setting temperatures must be used.

After heat setting in air under conditions of free shrinkage, the dye exhaustion first decreases and then increases with increasing setting temperature. The minimum exhaustion occurs after setting at around 160–190 °C (Figure 15.5). If applied tension prevents fabric shrinkage during heat setting, the dye uptake/temperature profile is similar to that under conditions of free shrinkage, but with higher uptake values. Heat setting changes the morphology of the polyester fibres. The effects on the dyeing rate and the extent of dyeing are variable depending upon the particular dye, the setting temperature and heating time, and the tension imposed.

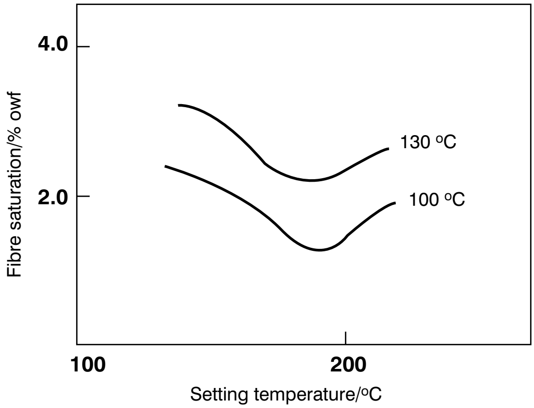


Figure 15.5 Influence of hot air setting temperature on dye uptake of polyester at dyeing temperatures of 100 and 130 °C

15.7.3 Carrier dyeing

There are obvious advantages to dyeing polyester fibres with disperse dyes at the boil, within a reasonable time, particularly for medium to deep shades. Unfortunately, this is only feasible with the most simple disperse dyes of low molecular weight. The more complex disperse dyes, which have the required fastness to heat setting and hot pressing and pleating, only diffuse extremely slowly into polyester fibres at 100 °C. One solution to this problem that avoids dyeing under pressure at temperatures above 100 °C is dyeing in the presence of a carrier.

A carrier is an organic compound, dissolved or emulsified in the dyebath, which increases the rate of dyeing. Carriers allow dyeing of even deep shades at the boil within a reasonable dyeing time. Common polyester dyeing carriers include butyl benzoate, methylnaphthalene, dichlorobenzene, diphenyl and o-phenylphenol, the latter two being the most popular. These are all aromatic compounds of low water solubility, so they are present in the dyebath as an emulsion. Typical commercial carriers therefore usually already contain anionic emulsifying agents.

A typical carrier dyeing procedure involves running the goods in the bath 60 °C and adding dilute dispersing agent, emulsified carrier and lastly the dispersed dyes. The temperature is then gradually raised to the boil and dyeing continued at this temperature. The sodium salt of o-phenylphenol is soluble in water and acidification liberates the insoluble phenol once dyeing has started. This ensures a fine emulsion. The usual effect of the carrier is to increase both the rate of dyeing and the dyebath exhaustion, but not in all cases. Benzoic acid, for example, decreases the exhaustion at equilibrium but increases the dyeing rate. Its effect is probably simply to increase the water solubility of the dye in the bath. Methylnaphthalene gives the best colour yield with many dyes at the lowest cost. During dyeing in certain machines, such as winches and jigs, a steam-volatile carrier may condense as a concentrated emulsion on colder internal surfaces. Drops of this condensed emulsion that fall onto the goods produce darker dyed spots. This can also occur if the carrier emulsion is not stable during dyeing and drops deposit on the fabric.

The actual mechanism by which a carrier accelerates dyeing has been widely debated and probably depends upon the carrier used. The polyester fibres absorb the carrier and swell. This swelling can impede liquor flow in packages causing unlevelness. The overall effect seems to be a lowering of the polymer glass transition temperature (T_g), thus promoting polymer chain movements and creating free volume. This speeds up the diffusion of the dye into the fibres. Alternatively, the carrier may form a liquid film around the surface of the fibre in which the dye is very soluble, thus increasing the rate of transfer into the fibre.

Incorporation of other monomers into the polyester also decreases the T_g value. Comonomers such as suberic acid (1,8-octanedioic acid) increase the polymer chain flexibility and give polyester fibres that can be dyed at 100 °C without a carrier. However, a polyester fibre, dyeable at the boil with disperse dyes of good heat fastness, without use of a carrier, and without any modification of the properties of regular PET, remains somewhat elusive. The new polytrimethylene terephthalate fibre (Corterra) is a step in response to this problem.

After dyeing, scouring of the goods removes most of the carrier. Any carrier remaining in the fibres invariably decreases the light fastness of the dyeing. Residual amounts of carrier vaporise during subsequent drying of the scoured fabric. Some carriers are quite volatile, have unpleasant odours and are toxic. Polyester dyeing carriers pose a serious environmental threat if present in the effluent or exhausted air. One of the easiest ways to eliminate o-phenylphenol is by mild alkaline washing, which dissolves this weakly acidic phenol.

Carrier dyeing has steadily declined since the development of suitable machines for dyeing polyester under pressure at temperatures around 130 °C. Carriers are still used in some garment and small commission dyehouses where high temperature pressurised dyeing machines are not available. The quantity of carrier required in dyeing decreases with increase in the dyeing temperature. The use of a small amount of carrier is useful for dyeing at 110–120 °C. Dyeing at this lower temperature leaches less oligomer from the polymer and better preserves the fibre bulk and elasticity. Carriers are also useful for dyeing wool/polyester blends when there is a risk of damaging the wool at dyeing temperatures above 100 °C. In this case, the carrier also helps to prevent cross-staining of the wool by the disperse dye.

Partial stripping of the colour of PET materials dyed with disperse dyes is usually possible by treatment with a solution of dyeing carrier or retarding agent at high temperature under pressure. Oxidative and reductive stripping are also possible but are likely to involve some undesirable effects upon the fabric handle or appearance. Prolonged treatment of polyester materials with alkaline solutions causes surface hydrolysis of ester groups and loss of weight. Once the surface has been degraded it is difficult to obtain the originally anticipated appearance.

15.7.4 High temperature pressure dyeing of polyester

As we have seen, the dyeing of polyester with disperse dyes at the boil is slow because of the low rate of diffusion of the dyes into the fibre. The activation energy for diffusion is quite high and raising the dyeing temperature from 100 to 130 °C considerably increases the rate of dye diffusion. Dyeing at this higher temperature under pressure, without a carrier, considerably increases the rate of dyeing and gives better coverage of filament irregularities because of the improved migration of the dyes. Dyeing is then also possible using higher molecular weight dyes, whose rates of diffusion at 100 °C are unacceptable. This permits production of dyeings with better fastness to light and to sublimation during permanent pleating. For those fabrics and yarns that lose bulk when dyed at 130 °C, dyeing at a lower temperature (110–120 °C) in the presence of some carrier is preferred.

The dyebath is usually set at pH 4.5–5.5 using either ammonium sulphate plus formic or acetic acid, or acetic acid alone. The weakly acidic dyebath ensures neutralisation of any residual alkali from scouring, which readily catalyses hydrolysis of the polyester, decreasing its strength. Reduction of some azo disperse dyes can occur during dyeing at high temperatures, while others undergo hydrolysis. These effects are minimal when dyeing in weakly acidic solution.

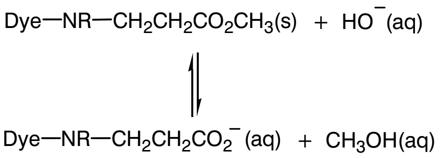
The concentrated dye dispersion is added to the bath at 50–60 °C. The bath may already contain a small amount of dispersant (0.5 g l^{-1}), if required. Lubricants in the dyebath avoid possible crack and crease marks in dyeing fabric in jet machines. The temperature of the bath is then slowly raised to 130 °C. A typical heating rate is about at 1.5 °C min^{-1}. Dyeing continues at the maximum temperature for about 60 min.

Each particular dyeing will have an optimum temperature/time profile, depending upon the type of goods, the machine being used and the dyes in the formula. A set of generalised dyeing conditions is used, however, provided that the dyebath exhaustion, the colour uniformity, and the shade reproducibility from batch to batch are acceptable. Dyeing times can be kept to a minimum by temperature control of the rate of exhaustion that gives uniform dye absorption. In this way, long levelling times at the maximum dyeing temperature are not needed. The dyeing time should be long enough for the dyes with the lowest dyeing rate to approach equilibrium. Disperse dyes do not generally interfere with each other and prevent their mutual absorption but they do have different dyeing rates. The dyeing rate is always higher at low dye concentrations in the bath. Some disperse dyes are deliberate mixtures of dyes of the same or different hue and about the same dyeing rate. They give fairly rapid dyeing because each dye is only present at low concentration.

PET fibre contains 1–4% of oligomers, mainly a cyclic trimer of ethylene terephthalate. It has a high melting point and is soluble enough in hot water during pressure dyeing to be extracted from the fibre. The oligomers also migrate to the PET fibre surface during steam heat setting, and to a lesser extent on dry setting. The oligomer can often be seen as a white dusty powder on the surface of the goods, or on the dyeing machine walls. Hydrolysis of oligomer deposits on machine surfaces by heating with an alkaline solution under pressure provides effective cleaning. Precipitated oligomer can cause nucleation of disperse dye crystal formation leading to coloured specks on the goods. In addition, oligomer particles reduce the rate of liquor flow through yarn packages and cause filament friction in spinning. The oligomer is much less soluble at temperatures below the boil. To avoid its precipitation once dyeing is concluded, the dyebath is drained at as high a temperature as possible, even above 100 °C. This can lead to problems in dyeing woven goods in rope form in jet machines since creases and crack marks can form while the polymer is still somewhat plastic. In these cases, draining at a lower temperature is necessary and the dyer must depend to a greater extent upon the subsequent rinsing and reduction clearing process to remove oligomer residues.

During dyeing, particularly of deep shades, there will invariably be some dye particles that adhere to the fibre surfaces, or are retained by yarns without penetration into the fibre. These mechanically held particles result in decreased fastness to washing, rubbing, sublimation and dry cleaning. Their presence also tends to dull the shade. Superficial dye particles can be detected by rinsing a dyed sample with a little cold acetone. This will dissolve the surface particles and produces a coloured solution but it does not remove any dye from within the PET fibres. For pale shades, scouring removes deposits of surface dye. Deep dyeings with disperse dyes on PET fibres will invariably require treatment by reduction clearing to give satisfactory crocking fastness. This process involves treatment with alkaline hydros (2 g l^{-1} NaOH, 2 g l^{-1} $Na_2S_2O_4.2H_2O$) and a surfactant (1 g l^{-1}) for 20 min at 70 °C. The reduction clearing temperature is well below the glass transition temperature of the polyester. The ionic compounds do not therefore penetrate into the fibres and only reduce the dye on the fibre surface. The reduction of azo disperse dyes is relatively easy but anthraquinone derivatives are more difficult to remove. The latter must be reduced and washed off the surface before re-oxidation occurs. The less soluble oxidised form is then held in suspension by the surfactant in the bath.

Some disperse dyes, originally from ICI (now available through DyStar), allow easy clearing of surface deposits. These are methyl esters of carboxylic acids that readily hydrolyse under alkaline conditions. The free carboxylic acids formed by hydrolysis are soluble in alkaline solution (Scheme 15.3). This allows clearing without a reducing agent. Since the alkali does not penetrate into the PET fibre at the clearing temperature, the dye within the fibres is unaffected.



Scheme 15.3

15.7.5 Polyester microfibres [4]

Microfibres of PET for production of fabrics with a lush handle are a fairly recent development. Microfibres have a fineness of less than 1.0 dtex per filament, an arbitrarily chosen value. Normal PET filaments are in the range 2–5 dtex. The introduction of microfibres has created a number of dyeing problems. Firstly, microfibres require more dye than regular denier fibres to achieve the same depth of shade (Section 10.4.4). The concentration of dye (% owf) required to achieve a given depth of shade is usually assumed to be inversely proportional to the square root of the filament fineness:

$$\frac{C_M}{C_R} = \frac{r_R}{r_M} = \sqrt{\frac{dtex_R}{dtex_M}} \qquad (1)$$

In this equation, C_M and C_R are the required concentrations of dye in the microfibre and regular denier fibre respectively, r_M and r_R the respective filament radii, and $dtex_M$ and $dtex_R$ the respective filament fineness. This approximate relationship predicts that a 0.5 dtex microfibre will require $(2.5/0.5)^{1/2}$ or about 2.2 times as much dye in the fibre to give the same depth of shade as a 2.5 dtex filament. It only applies, however, when the regular and microfibres being considered are identical in all other properties. In fact, it is the dyeing rate that should be proportional to the available filament specific surface area ($m^2\ g^{-1}$) and therefore inversely proportional to the filament radius and to the square root of the filament decitex. The value of the diffusion coefficient of the dye in the fibre does not change when the filaments are finer.

Secondly, because of the more rapid uptake of dye by microfibres, level dyeing requires greater control. The greater specific surface area of microfibres also means that dye desorption during washing is more rapid and the washing fastness is less than for fabrics made of conventional filaments. Dyed microfibre fabrics also have lower fastness to light at equal apparent depth. In addition, the closeness of microfibre packing in yarns makes wetting and yarn penetration difficult. Nevertheless, the lush handle and special surface effects that are possible for fabrics made of microfibres have ensured their success.

15.7.6 The Thermosol process

The Thermosol process is a continuous dyeing process introduced by Du Pont in 1949. A dispersion of the disperse dyes is padded onto the polyester fabric. The material is then dried using a hot flue air dryer or by infrared radiation, the latter usually giving much less migration of the dye. The use of a migration inhibitor in the pad bath is usually recommended. Even then, dye migration during drying of materials of 100% polyester is difficult to eliminate and such materials tend to dye more deeply on the yarn surface. Final drying of the padded material takes place using heated cylinders. Section 10.5 discusses padding and migration in continuous dyeing.

The dry fabric is then heated in air, or by contact with a hot metal surface, to a temperature in the range of 190–220 °C for 1–2 min. In hot air, at least 50% of the time is for heating the polyester to the maximum temperature. The specific conditions depend on the type of equipment, the dyes and the fabric. As the fabric approaches the maximum temperature, the disperse dyes begin to sublime and the polyester fibres absorb their vapours. (Sublimation is the transformation of a solid directly into a gas without forming the liquid phase. A common example is the evaporation of ice on a cold day.)

At about 200 °C, sublimation of the solid dye, transfer of its vapour into the fibres, and penetration into the fibres by diffusion are all quite rapid. Commercial disperse dyes for the Thermosol process are usually classified according to their ease of transfer by sublimation. This is related to the their fastness to heat in hot pressing and pleating. It is imperative that as much of the vaporised dye as possible be absorbed by the polyester fibres. If the rate of sublimation is too low, dye particles will remain in the fibre matrix and the colour yield will be low. When the rate of sublimation is too high, the dye vapour builds up faster than it can be absorbed by the polyester and escapes from the proximity of the fibres, usually depositing on the machine walls. The temperature and time of heating must therefore be carefully controlled to provide the appropriate rate of sublimation and the optimum colour yield.

Despite the simple dyeing mechanism, there are a number of technical problems that can result in inferior dyeings. The fabric must initially contain a uniform distribution of dye particles if the final dyeing is to be level. Therefore, uniform dispersion and padding are crucial. Migration must be minimised, particularly if it leads to more dye on one face of the fabric than the other. During the sublimation stage, it is essential to provide conditions that allow a balance between the rate of dye vaporisation and absorption of the vapour by the fibres. The Thermosol process is widely used for narrow fabrics of 100% PET such as ribbons and belts. The vapour dyeing technique also applies to transfer printing, discussed in Section 23.8.

The Thermosol method is popular for dyeing the polyester component in cotton/polyester fabrics [5]. In this case, the absorbent cotton fibres in the fabric hold almost all the initial dye dispersion padded onto the material. This helps to reduce dye migration during drying. During subsequent heating, the dye vaporises and transfers from the cotton into the polyester fibres. Since two types of fibres are being continuously dyed, each with a separate fixation step, the dyeing ranges for cotton/polyester materials tend to be very complex (Figure 10.7). Both the dyes for the polyester and for the cotton are initially padded onto the fabric. The polyester is dyed in the Thermosol unit. After additional padding of the cooled fabric with a solution of the other required chemicals for dyeing the cotton, it passes through a steamer. This promotes diffusion and fixation of dyes on the cotton. The second pad contains NaOH and salt solution for dyeing with reactive dyes (Chapter 16), NaOH and $Na_2S_2O_4$ for vat dyes, NaS or NaSH for sulphur dyes (Chapter 17), and simply salt solution for direct dyes (Chapter 14). A thorough washing of the dyed fabric completes the process. This includes rinsing, an oxidation step in the case of vat and sulphur dyes, soaping to remove surface colour and final rinsing.

15.7.7 Classification of disperse dyes for polyester

Disperse dyes for a compound shade on polyester can have quite incompatible dyeing properties. The SDC classification of disperse dyes is based on migration ability during exhaust dyeing, colour build-up, sensitivity to changes in temperature and the rate of dyeing [2].

This type of dye is often classified on the basis of dyeing rate and sublimation fastness, particularly for polyester dyeing. These two properties are a function of

Table 15.2 Classification of disperse dyes for polyester

Classification	Molecular weight	Polarity	Dyeing rate	Sublimation fastness
Low energy	Low	Low	High	Low
Medium energy	Moderate	Moderate	Moderate	Moderate
High energy	High	High	Low	High

molecular weight and the number of polar groups in the dye molecule. Table 15.2 shows the most common classification. It applies to the dyeing of acetate, of polyester with or without carrier, and of polyester/cotton, but is somewhat arbitrary.

Most dyeing and fastness properties change gradually with increase in molecular size. Small dye molecules with low polarity are levelling, rapid dyeing dyes with poor heat resistance. These are called low energy disperse dyes. More polar, higher molecular weight dyes have low dyeing rates, poor migration during dyeing but good heat and sublimation fastness. These constitute the high energy disperse dyes. The development of disperse dyes of improved sublimation fastness required dye molecules with relatively polar and hydrophilic substituents to reduce their vapour pressure at high temperatures. This promotes somewhat higher solubility in water but the increase in molecular size reduces the dyeing rate at a given temperature. The high energy disperse dyes are those requiring a higher Thermosol temperature. The light fastness does not depend on the molecular size.

Dyes in a mixture are usually selected from the same energy class. Build-up of the colour on shade requires that the dyes all have about the same dyeing rate. Testing of dye recipes is essential because many disperse dyes, even dyes of the same dyeing group, are incompatible in mixtures. This is true even though they may have the same dyeing rates and build-up properties when tested separately. The dye manufacturers provide considerable information assisting the dyer to select appropriate dyes for a given application.

15.7.8 Dyeing modified polyesters

A variety of modified polyester fibres are available that can be dyed with disperse dyes, and other types of dyes, at temperatures not exceeding 100 °C. The so-called non-carrier types can be dyed with disperse dyes at the boil, although very deep shades may require a small amount of carrier. The basic polymer is PET but contains a comonomer with a more flexible molecular chain such as suberic acid (1,8-octanedioic acid). The polymer has a more open molecular structure, a lower T_g and dye penetration is therefore easier. The new polytrimethylene terephthalate fibre (Corterra) also has a lower T_g than PET and can be dyed with disperse dyes in a bath at the boil under normal pressure.

Polyester modified to have anionic sites contains comonomers such as 5-sulpho-isophthalic acid (Section 4.3.3). It is readily dyed with disperse dyes, and with cationic dyes. These types of modified polymer are also more easily hydrolysed. Therefore, during processing, the pH of solutions must not be excessive and the maximum pressure dyeing temperature should not be above 120 °C. Additions of Glauber's salt to the dyebath protect basic dyeable polyester fibres from hydrolysis. Modified polyester fibres are also more sensitive to heat setting before dyeing, the maximum setting temperature being around 180 °C.

Cationic dyes require some acetic acid in the dyebath and dyeing at pH of 4–5 at 100–120 °C is typical. The brightly coloured dyeings with cationic dyes have good fastness to washing and light. Combinations of regular and basic dyeable polyester can be dyed with mixtures of cationic and disperse dyes to produce two colour effects. The carpet industry is a major outlet for this type of fibre. The new polyester fibre poly(trimethylene terephthalate) produced from terephthalic acid and 1,3-propanediol, rather than the usual 1,2-ethanediol, is also initially intended for use in carpets.

15.8 DYEING OF OTHER SYNTHETIC FIBRES

Acrylic fibres can be dyed with disperse dyes but the extent of dye absorption is limited and the colour build-up is poor. Dyeing at temperatures above 100 °C to solve this problem is not possible because of the plasticity and excessive shrinkage of this type of fibre. Disperse dyes on acrylics have good levelling and good fastness properties. They give dyeings of better washing fastness on acrylic fibres than on nylon and there is no gas fume fading problem. Acrylic materials are quite plastic at high dyeing temperatures and rapid cooling of the dyebath may set creases in the fabric. On the other hand, slow cooling may deposit non-absorbed dye particles on the fabric surface and scouring may be needed after dyeing to clean the surface. Unfortunately, the application of disperse dyes on acrylic fibres is limited to rather pale shades.

Segmented polyurethane elastomeric fibres (Lycra) are finding increasing application in a wide variety of products in which they are blended with other fibres. This type of fibre is sensitive to alkaline hydrolysis and severe alkaline scouring must be avoided. Lycra is frequently found in nylon fabrics and both fibres will absorb disperse dyes but not necessarily to the same extent. Like nylon, polyurethanes can also be dyed with acid dyes.

Polypropylene fibres have little substantivity for any of the usual types of dye. These fibres are extremely hydrophobic. They will absorb a limited amount of disperse dyes to give pale dyeings of poor washing fastness. Dye penetration is difficult because the polymer is very crystalline, has a compact structure, and has no polar groups for interaction with dye molecules.

Several chapters in the book ‘The Dyeing of Synthetic Polymer Fibres’, edited by Nunn [6], provide somewhat dated but still useful information on dyeing synthetic fibres with disperse dyes.

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CHAPTER 16

Reactive dyes

16.1 THE DEVELOPMENT OF REACTIVE DYES

Dyeings of cotton with direct dyes (Chapter 14) have rather poor washing fastness because only weak polar and dispersion forces bind the dye molecules to the cellulose polymer chains. Direct dye molecules can therefore easily diffuse out of the cotton during washing. The best fastness to washing requires precipitating an insoluble pigment and mechanically trapping it within the cotton fibres. This type of dyeing process with vat and azoic dyes is, however, much more complicated than direct dyeing (Chapters 17 and 19).

The idea of immobilising a dye molecule by covalent bond formation with reactive groups in a fibre originated in the early 1900s. Various chemicals were found that reacted with the hydroxyl groups of cellulose and eventually converted into coloured cellulose derivatives. The rather forceful reaction conditions for this led to the false conclusion that cellulose was a relatively unreactive polymer. Possibly because of this, a number of dyes now known to be capable of covalent bond formation with groups in wool and cotton were not initially considered as fibre-reactive dyes, despite the good fastness to washing of their dyeings.

In 1955, Rattee and Stephen, working for ICI in England, developed a procedure for dyeing cotton with fibre-reactive dyes containing dichlorotriazine groups. They established that dyeing cotton with these dyes under mild alkaline conditions resulted in a reactive chlorine atom on the triazine ring being substituted by an oxygen atom from a cellulose hydroxyl group (Figure 1.5). This is shown in Scheme 16.1 where Cell–OH is the cellulose with a reactive hydroxyl group, Dye–Cl is the dye with its reactive chlorine atom, and Cell–O–Dye the dye linked to the cellulose by a covalent bond. The role of the alkali is to cause acidic dissociation of some of the hydroxyl groups in the cellulose, and it is the cellulosate ion (Cell–O$^-$) that reacts with the dye.

$$\text{Cell—OH} + \text{HO}^- \rightleftharpoons \text{Cell—O}^- + \text{H}_2\text{O}$$

$$\text{Cell—O}^- + \text{Dye—Cl} \longrightarrow \text{Cell—O—Dye} + \text{Cl}^-$$

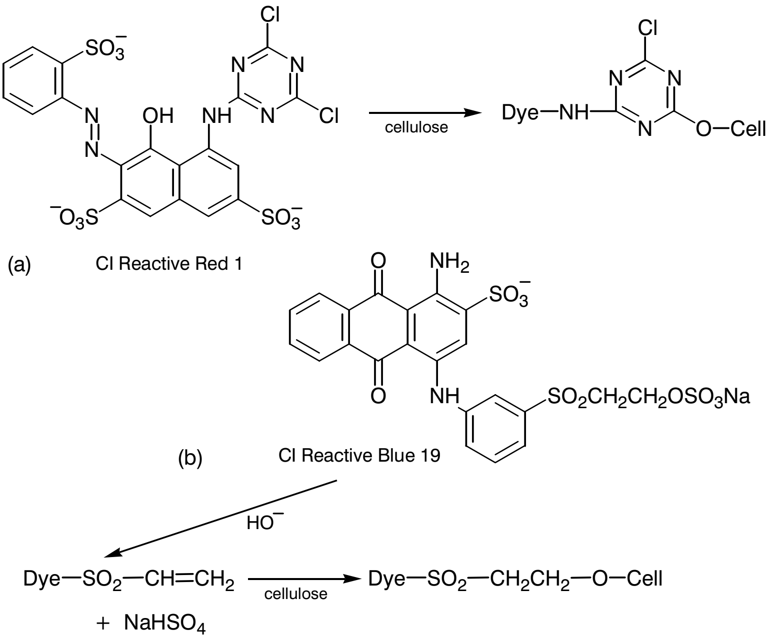
Scheme 16.1

The dyeings had very good fastness to washing. The only way the fixed dye can bleed from the cotton is after hydrolysis of the covalent bond between the dye and the cellulose. This requires conditions more forceful than those met with in ordinary washing in hot water. Within about five years of this important development, all the major dyestuff manufacturers were marketing reactive dyes for cotton, and also for wool. Reactive dyes, particularly those used for dyeing cotton, have become one of the major classes of dye because of their good washing fastness, their bright shades and their versatile batch and continuous dyeing methods.

16.2 REACTIVE DYES FOR COTTON [1]

16.2.1 Structures of reactive dyes for cotton

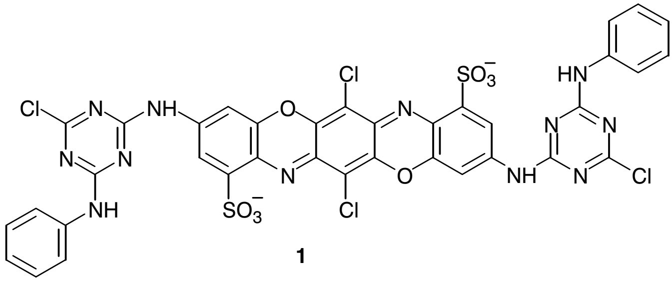
The molecular structures of reactive dyes resemble those of acid and simple direct cotton dyes, but with an added reactive group. Typical structures include the azo (Figure 16.1, (a)), anthraquinone (Figure 16.1, (b)), triphenodioxazine (**1**, in Figure 16.2) or copper phthalocyanine chromophores (**2**). The key structural



(a) CI Reactive Red 1

(b) CI Reactive Blue 19

Figure 16.1 Nucleophilic substitution (a) and addition reactions (b) of reactive dyes with cellulose



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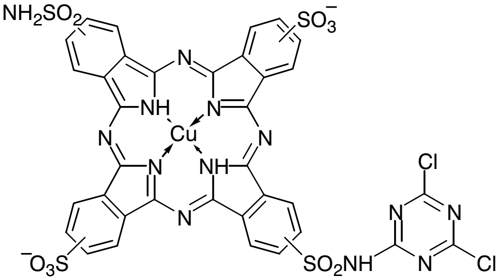

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Figure 16.2 Triphenodioxazine (**1**) and copper phthalocyanine reactive dyes (**2**)

features of a reactive dye are the chromophoric system, the sulphonate groups for water solubility, the reactive group, and the bridging group that attaches the reactive group either directly to the chromophore or to some other part of the dye molecule. Each of these structural features can influence the dyeing and fastness properties.

Most commercial ranges of reactive dyes have a complete gamut of colours, many of which are particularly bright. Reactive dyes often have quite simple structures that can be synthesised with a minimum of coloured isomers and biproducts that tend to dull the shade of the more complex polyazo direct dyes. Some colours are difficult to obtain with simple chromophores. Dark blue and navy reactive dyes are often rather dull copper complexes of azo dyes and the production of bright green reactive dyes remains a problem.

A wide range of possible fibre-reactive groups has been examined and evaluated by the dyestuff manufacturers. The final choices for commercial dyes are limited by a number of constraints. The reactive group must exhibit adequate reactivity towards cotton, but be of lower reactivity towards water that can deactivate it by hydrolysis. The hydrolysis of the dye's reactive group is similar to its reaction with cellulose but involves a hydroxyl ion in water rather than a cellulosate ion in the fibre (Scheme 16.2). In addition, the dye–fibre bond, once formed, should have adequate stability to withstand repeated washing. Other factors involved are the ease of manufacture, the dye stability during storage and the cost of the final reactive dye.

$$\mathrm{HO^- + Dye{-}Cl \longrightarrow Dye{-}OH + Cl^-}$$

Scheme 16.2

Reactive groups are of two main types:

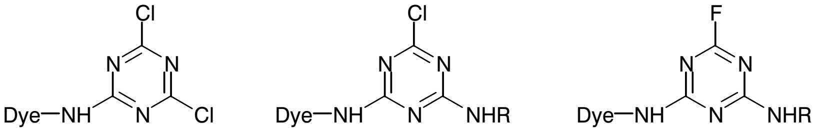
(1) those reacting with cellulose by nucleophilic substitution of a labile chlorine, fluorine, methyl sulphone or nicotinyl leaving group activated by an adjacent nitrogen atom in a heterocyclic ring (Figure 16.1, (a));

(2) those reacting with cellulose by nucleophilic addition to a carbon–carbon double bond, usually activated by an adjacent electron-attracting sulphone group. This type of vinyl sulphone group is usually generated in the dyebath by elimination of sulphate ion from a 2-sulphatoethylsulphone precursor group with alkali (Figure 16.1, (b)).

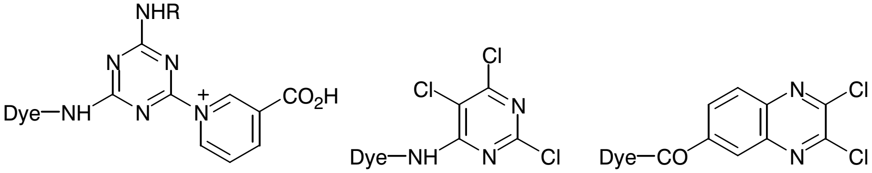
Although many of the early reactive dyes had only one reactive group in the dyestuff molecule, many of the newer reactive dyes are bifunctional with two or more identical or different reactive groups (Section 16.4). Figure 16.3 shows some typical fibre-reactive groups and the commonly used abbreviations for these groups. Dyes with nicotinyltriazine reactive groups (NT) will react with cotton on heating under neutral conditions.

16.2.2 Basic principle of dyeing cotton with reactive dyes

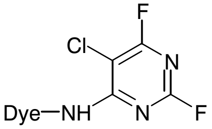
The relatively simple procedure for batch dyeing of cotton materials with reactive dyes, developed by Rattee and Stephen, is still used for all types of reactive dyes irrespective of their particular reactive group. Dyeing is commenced in neutral solution, often in the presence of salt to promote exhaustion of the dye onto the cotton. During this period, the dye does not react with the fibre and migration from fibre to fibre is possible. Then, an appropriate alkali is added to the dyebath to increase its pH. This initiates the desired dye–fibre reaction. The hydroxyl groups in cellulose are weakly acidic and absorption of hydroxide ions causes some dissociation, forming cellulosate ions. It is these that react with the dye by



Dichlorotriazine (DCT) Monochlorotriazine (MCT) Monofluorotriazine (MFT)



Nicotinyltriazine (NT) Trichloropyrimidine (TCP) Dichloroquinoxaline (DCQ)



Difluorochloropyrimidine (DFCP)

$Dye{-}SO_2{-}CH{=}CH_2$

Vinylsulphone (VS)

Figure 16.3 Typical fibre-reactive groups in commercial reactive dyes

nucleophilic addition or substitution (Figure 16.1). In general, the lower the reactivity of the reactive group of the dye towards the alkaline cellulose, the higher the final dyeing temperature and the higher the final pH of the dyebath.

Unfortunately, under the alkaline conditions necessary for the dye–fibre reaction, hydroxide ions also react with the reactive group of the dye in much the same manner as the cellulosate ion. This produces the hydrolysed dye, which is incapable of reaction with the fibre. Hydrolysis of the dye is slower than the reaction with the alkaline cotton but it is significant and reduces the efficiency of the fixation process. After dyeing, any unreacted and hydrolysed dye present in the cotton must be removed by thorough washing. This ensures that no colour will bleed from the cotton on subsequent washing during use. The higher the substantivity of the reactive dye for the cotton, the more difficult it is to wash out unfixed dye from the material. Many of the first reactive dyes had quite simple molecular structures and low substantivity for cotton, so that the removal of hydrolysed dye from the material by washing was relatively easy. This is not necessarily true for reactive dyes of more complicated molecular structure.

16.2.3 Dye reactivity, application and storage

The reactive groups of the various types of reactive dye have different chemical structures and show a wide range of reactivities. They were originally divided into cold- and hot-dyeing types but many current ranges would be better called warm-dyeing. The most reactive types, such as DCT reactive dyes (Figure 16.3), are applied at lower temperatures (20–40 °C) and only require a weak alkali such as $NaHCO_3$ or Na_2CO_3 for fixation. The less reactive types, such as MCT dyes, need higher temperatures (80–90 °C) and stronger alkalis such as Na_2CO_3 plus NaOH. Many dyestuff manufacturers now market several ranges of reactive dyes for cotton, each with its own particular recommended dyeing procedure. Table 16.1 gives some typical examples based on the type of reactive grouping.

Table 16.1 Reactive groups used in commercial reactive dyes

Reactive group	Commercial name	Reactivity	Exhaust dyeing temperature (°C)
DCT	Procion MX (BASF)	high	25–40
MCT	Procion H (BASF) Basilen (BASF) Cibacron (Ciba)	low	80–85
MFT	Cibacron F (Ciba)	moderate	40–60
DCQ	Levafix E (DyStar)	low	50–70
DFCP	Drimarene K (Clariant) Levafix E-A (DyStar)	moderate to high	30–50
VS	Remazol (DyStar)	moderate	40–60
TCP	Drimarene X (Clariant)	low	80–95
NT	Kayacelon React (Nippon Kayaku)	moderate to high	100–130 *

* React under neutral conditions

Because most reactive dyes are prone to hydrolysis, their handling and use requires care. Most are readily water-soluble and the dye solution is prepared in the usual way by pasting with water and then adding more water. The temperature of the water used depends upon the ease of solution and the reactivity of the dye. Hot water is not recommended for dissolving dyes of high reactivity, because of the risk of hydrolysis of the reactive group, but is suitable for the less reactive types. Once the dye solution has been prepared, it cannot be stored for later use without some risk of hydrolysis of the reactive group. This decreases its fixation ability and is a particular problem with the most reactive types of dye. Dyes containing a 2-sulphatoethylsulphone group, however, can be dissolved in neutral water at the boil without risk of hydrolysis. Formation of the reactive vinyl sulphone group (Figure 16.1, (b)) requires the addition of alkali.

Reactive dyes for printing are usually dyes of low reactivity so that the print paste can be stored for some time at room temperature without deterioration from hydrolysis of the reactive group. Reactive dyes of low reactivity and relatively high substantivity are valuable for dyeing using long (high) liquor ratios, using a winch machine. Exhaust dyeing with low reactivity dyes at the higher temperatures required for fixation allows better penetration of the dyes into the cotton fibres. For continuous dyeing with reactive dyes stabilised liquid forms are available. Although these contain special pH buffers and stabilisers to minimise the hydrolysis reaction, they only have a limited shelf life.

Many commercial reactive dyes are dusty powders but all physical forms must be handled with care. These dyes react with the amino groups in proteins in the skin and on mucous surfaces. Inhalation of the dust is dangerous and a dust mask is obligatory during handling. Reactive dye powders and grains are sometimes hygroscopic and drums must be carefully re-sealed. Most reactive dyes have a limited storage period, after which some deterioration can be expected. Standardisation and comparison of reactive dye powders or liquids cannot be done by the usual spectrophotometric procedure involving absorbance measurements of standard solutions (Section 24.2). Both the reactive dye and its hydrolysed form are equally coloured, but only the former is capable of reaction with the cellulose during dyeing. Therefore, dyeings must be prepared and their colours compared with standard dyeings. Chromatographic techniques usually allow separation and quantitative measurement of the relative amounts of a reactive dye and its hydrolysis product in a given dye (Section 24.5).

16.2.4 Fastness properties of reactive dyes on cellulosic fibres

In general, reactive dyes on cellulosic fibres give dyeings with good to very good fastness to washing and other wet processes. Apparent inferior fastness to washing is usually because of incomplete removal of unreacted and hydrolysed dye from the material by washing after dyeing. The presence of unfixed dye can easily be tested for by hot pressing a wet sample of the dyeing sandwiched between two pieces of dry white cotton. Colour transfer to the white material indicates the presence of unfixed dye in the dyeing. It is more likely to be a problem for deep dyeings.

The use of reactive dyes is growing rapidly, faster than for any other dye application class. This is because these dyes also give dyeings of moderate to good light fastness, allow relatively simple and diverse dyeing methods and are available in a range of bright colours. They have contributed significantly to the decline of direct cotton dyes. Their fastness properties, though generally good, do not match those of pigmented cotton dyed with vat dyes. In particular, the fastness to bleaching by chlorine, and to a lesser extent by peroxides present in modern household detergents, is often only moderate.

16.2.5 Evidence for covalent bond formation with cellulose

The good fastness to washing of dyeings with reactive dyes on cellulosic fibres is a consequence of the stable covalent bond formed between the dye's reactive group and the cellulose polymer. There is considerable evidence to support the formation of this dye–fibre bond. Dyeings are resistant to colour stripping with hot aqueous pyridine, a solvent that effectively removes direct dyes from cotton. Dyeings of cotton obtained with bifunctional dyes often exhibit reduced swelling and decreased solubility in cuprammonium solution. A dye molecule with two reactive groups crosslinking two different cellulose chains would explain this. If the colour of a dyeing obtained with an azo reactive dye is destroyed by chemical reduction with alkaline sodium hydrosulphite, which cleaves the azo dye into two primary aromatic amines, the amine remaining attached to the cellulose can be diazotised and coupled with an appropriate phenol to reform a coloured fibre. Finally, bacterial degradation of reactive dyed cotton that depolymerises the cellulose, but avoids breaking the dye–fibre bond, gives coloured products containing the original dye still bonded to glucose.

16.3 BATCH DYEING OF COTTON WITH REACTIVE DYES

16.3.1 Preparation for dyeing

Level well-penetrated dyeings require careful preparation of the material. All sizing compounds capable of reacting with the dye, such as starch or polyvinyl alcohol, must be removed from the material and any traces of residual alkali must be uniformly neutralised. Good alkali boiling to remove wax is essential for goods to be dyed with cold-dyeing reactive dyes because penetration of the dyes into the fibres is much more difficult at lower dyeing temperatures. Reactive dyes often give such bright colours that bleaching may not be necessary. Once size has been removed, grey cotton goods can sometimes be simultaneously scoured and dyed using hot-dyeing reactive dyes and an efficient detergent. Because of the sensitivity to bleaching by chlorine of some reactive dyes, over-chlorinated water must be avoided or treated with a reducing agent such as sodium bisulphite or thiosulphate.

16.3.2 The three-step exhaust dyeing process

A typical exhaust dyeing process for cellulosic materials using reactive dyes has three distinct phases:

(1) the initial exhaustion phase. Dyeing is started in neutral solution so that there is little likelihood of the dye reacting with the cellulose. During this stage of dyeing, some reactive dye will be absorbed by the fibres, the amount depending upon its substantivity. This dye is capable of migration to promote level dyeing. Sodium chloride or sulphate will often be present initially or be added gradually to the dyebath during this phase to promote exhaustion. The temperature of the dyebath may also be gradually increased to aid penetration of dye into the fibres and to assist migration;

(2) the fixation phase. After the initial exhaustion phase, the pH of the dyebath is increased by complete or gradual addition of the appropriate type and amount of alkali. This causes dissociation of some of the hydroxyl groups in the cellulose and the nucleophilic cellulosate ions begin to react with the dye. The fixation process then results in additional dye absorption, to re-establish the dyeing equilibrium. Dye absorption from solution and reaction with the fibre then progress until no further dye is taken up. Figure 16.4 illustrates the variations of the dyebath exhaustion and the extent of fixation during a typical exhaust dyeing;

(3) the post-dyeing washing. The rinsed dyeing contains dye bonded to the cellulose, absorbed but unreacted dye, as well as hydrolysed dye. There will also be residual alkali and salt. The latter are relatively easy to remove by successive rinsing in cold and then warm water. As much unfixed dye as possible must be washed out of the dyeing. If this is not done, desorption of this dye during washing by the consumer can cause staining of other materials in the wash. Some unfixed dye is eliminated during the initial rinsing that removes salt and alkali. Thorough washing of the dyeing using a boiling detergent solution (soaping) eliminates the remainder. The dyeing is then finally rinsed in warm water. Soaping must often be repeated for deep dyeings or the residual unfixed dye must be complexed with a cationic agent (Section 16.3.5).

Reactive dyes are very versatile and allow a variety of different approaches for controlling the rate of dye absorption, and the degree of dye migration and dye fixation. Salt additions, temperature variations and alkali additions are used alone or in combination to control the dyeing process. Reactive dyes have recently been classified as [1]:

(1) alkali-controllable dyes, which have relatively high reactivity and only moderate substantivity. They are applied at relatively low temperatures and level dyeing requires careful control of the addition of alkali to initiate the fixation stage. Examples include DCT, DFCP and VS reactive dyes;

(2) salt-controllable dyes. These are dyes of relatively low reactivity towards cotton under alkaline conditions and therefore the dyeing temperature will be as high as 80 °C. They have appreciable substantivity and level dyeing requires careful addition of salt to promote exhaustion. Examples in this class include TCP, MCT as well as MFT reactive dyes;

(3) temperature-controllable dyes, which undergo fixation at high temperatures even under neutral conditions. The NT dyes are in this class.

The objective of dyeing with reactive dyes is to obtain the maximum degree of reaction between the dye and fibre, with a minimum of dye lost through hydrolysis of the reactive group, and under conditions where the colour of the dyed material is uniform. Dyes with different reactive groups and molecular structures require different amounts of added salt to obtain economical exhaustion. Some reactive dyes, including most of the oldest, have relatively simple molecular structures and quite low substantivity for cellulosic fibres. They need high concentrations of salt, up to 100 $g\ l^{-1}$, particularly when dyeing deep shades or using long (high) liquor ratios. At such high salt concentrations, there is always a risk of dye precipitation, particularly when dyeing at low temperatures. Although Glauber's salt is more expensive than sodium chloride, it is preferred for dyes prone to aggregation at low dyeing temperatures, such as the turquoise copper phthalocyanine reactive dyes. The advantage of dyes with low substantivity is that they diffuse easily in the fibres and are easy to wash out of the material after dyeing. The higher the substantivity of the reactive dye for the cellulose, the higher the bath exhaustion and the greater the chance of reaction with the fibre, but the greater the difficulty of removing unfixed dye during the final washing.

For dyeings with vinyl sulphone dyes, it is advisable to ensure that the residual alkali has been removed or neutralised prior to soaping since hydroxide ion can catalyse hydrolysis of the ether type dye–fibre bond and result in additional colour bleeding from the goods (Scheme 16.3). Dyeings with vinyl sulphone dyes have maximum dye–fibre bond stability at around pH 4.5, whereas the corresponding value for dyes based on halogenated nitrogen heterocycles is 6–7. The latter type have dye–fibre bonds that are more sensitive to acid-catalysed hydrolysis.

$$\text{Dye—O—Cell} + H_2O \longrightarrow \text{Dye—OH} + \text{Cell—OH}$$

Scheme 16.3

The dyeing temperature and the nature and concentration of the alkali required are determined by the reactivity of the dye, its degree of sulphonation and its substantivity. For tightly twisted yarns and compact woven fabrics, the migration phase of dyeing with low reactivity dyes can be carried out at higher temperatures up to 120 °C to promote initial migration and penetration into the textile. This is well above the later fixation temperature in the presence of alkali (80 °C). Azo copper complex dyes will not withstand these conditions and tend to loose the copper ion. For a higher fixation temperature, reaction with the fibre occurs at lower pH, using a weaker alkali or a lower concentration of the usual alkali. As is the case for salt addition, a deeper shade, or a higher liquor ratio, will require more alkali. It is not usual to exceed a dyebath pH of 11, even with the less reactive dyes since this invariably leads to lower colour yields because of dye hydrolysis.

The effects of increasing the dyeing pH during the fixation phase are complex but usually involve an increase in the rates of reaction of the dye with the fibre and with hydroxide ion. For polysulphonated dyes, one effect of dyeing at pH above 11 is the decrease in substantivity of the dye for the increasingly anionic dissociated cellulose. The greater negative charge of more cellulosate ions repels the dye anions. In fact, some dyes actually desorb from the fibre into the dyebath when the alkali is added at the start of the fixation stage giving a sudden decrease in the degree of exhaustion at that point. In addition, with polysulphonated dyes, the substantivity decreases as dye fixation proceeds because the cotton contains more and more bound anionic dye molecules, which also repel the unfixed dye. These effects can be counteracted by an increased concentration of salt in the dyebath.

Dye hydrolysis is more pronounced and exhaustion is less at high liquor ratios. Therefore, in winch dyeing, reactive dyes of higher substantivity are preferred. In recent years, there has been a considerable shift to dyeing with reactive dyes on machines with low liquor ratios. This gives more efficient dyeing, and reduces the consumption of dyes, salt and alkali. Figures 16.4 and 16.5 allow comparison of typical dyeing procedures in which the alkali for fixation is added to the dyebath in one portion (Figure 16.4), or gradually using a variable speed metering pump (Figure 16.5). For the latter method, the rates of exhaustion and fixation are relatively constant.

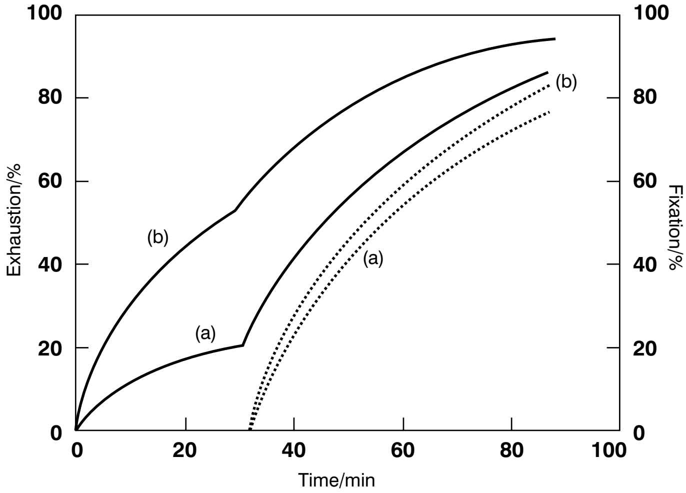


Figure 16.4 Dyebath exhaustion (solid line) and dye fixation (dotted line) as a function of time during dyeing with low (a) and high substantivity (b) reactive dyes; alkali addition at 30 min

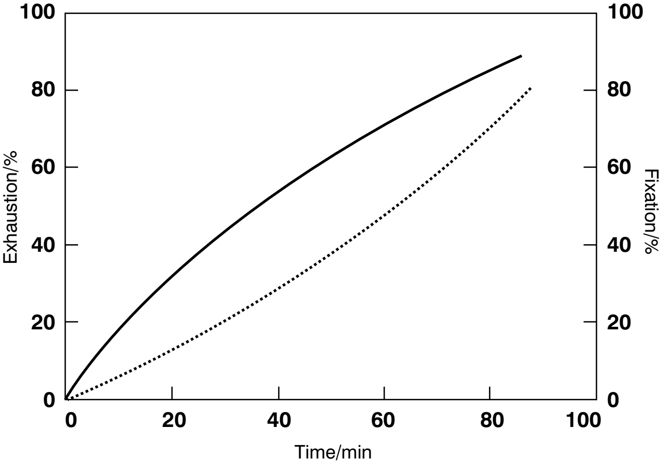


Figure 16.5 (See also Figure 10.3) Dyebath exhaustion (solid line) and dye fixation (dotted line) as a function of time during dyeing with a reactive dye, with metering of the alkali solution

Viscose fibres give higher fixation and exhaustion of reactive dyes than cotton. In fact, for identical conditions, exhaustion and fixation increase in the order: cotton, mercerised cotton, viscose. The washing fastness of reactive dyes on viscose is also somewhat better than on cotton. Because of the ease of swelling of viscose, the dyeing pH and temperature for a given dye may be different than for cotton, particularly if dye penetration may be problematic.

The so-called ‘all-in’ dyeing method has the advantage that no additions are required during dyeing and is therefore the most rapid dyeing method. The goods are run in the filled machine with all the added salt and alkali and the reactive dye solution then added over 10–15 min. The rate of dye fixation is controlled by gradual heating. The starting temperature and heating gradient must be well controlled for good colour reproducibility. The NT reactive dyes, mixed with disperse dyes, are useful for dyeing cotton/polyester at 130 °C under neutral conditions.

16.3.3 Washing-off of unfixed reactive dyes

Removal of hydrolysed and unreacted dye from the goods is a vital step after dyeing. The amount of unfixed dye remaining in a cotton fabric dyed with reactive dyes may have to be less than 0.002% owf. Although bleeding out of such a small amount during subsequent washing by the consumer will not significantly alter the depth of shade of the material, it can visibly stain adjacent white goods. This is usually unacceptable.

Both batch and continuous washing processes involve three stages. Initially, the goods are rinsed in cold and warm water. This is a dilution stage aimed at removing as much salt and alkali from the goods as possible. This makes the next soaping stage much more efficient since at lower electrolyte concentrations the substantivity of the dye is less, making its desorption easier. The final stage is again a warm rinsing stage to dilute the final dye solution adhering to the fibres to the point that the amount of unfixed dye carried over to the final drying is minimal. This residual quantity of dye will be deposited on the fibre surface on evaporation of the water during drying and will be easily removed by later washing. Obviously, the amount must be as small as possible.

The entire washing operation involves achieving a compromise between the effectiveness of removal of unfixed dye and the cost of the large volumes of water used, including the heating costs. Low liquor ratio washing saves water but gives less dilution of the washing liquors. Some dyeing machines allow overflow rinsing but this consumes much more water. For winch and jig dyeing machines operating at atmospheric pressure, it is not possible to carry out soaping at temperatures above 90 °C, even when they are closed. For any given dyeing machine, each rinsing and washing stage should be evaluated and a general satisfactory washing protocol established. One point requires particular attention. After each stage in the washing cycle, dye transfers from one bath to the next, in the solution retained by the fabric. This transfer must be as low as possible. This means that machines should be completely drained between stages, and wash boxes in continuous washing must have effective mangles to squeeze out as much solution as possible from the fabric leaving the box.

16.3.4 Dyeing compatibility of reactive dyes

Ideally, reactive dyes in a mixture should all exhaust and react with the fibre at about the same rate so that the shade builds up on tone. Dyes from different ranges, with different reactive groups, can rarely be used together because of their different dyeing characteristics and reactivities. It is therefore usual to mix dyes with the same type of reactive group having about the same substantivity. Since there is often a great deal of uncertainty about the particular type of reactive group in a given reactive dye, dye selection must often be from one particular manufacturer's dye range and based on his recommendations.

Compatible dyeing behaviour is a function of all the process variables and requires careful control of the dyeing temperature, salt and alkali concentrations, the dyeing time and the liquor ratio. Once the dye has reacted with the cellulose, it is completely immobilised and cannot migrate. Control of the process variables determines whether a given shade will be reproducible from batch to batch. When dyeing with mixtures of reactive dyes, shading is usually possible by addition of low substantivity dyes to the alkaline bath. The dyebath may be partially drained and re-filled with cold water, the solution of shading dyes added and the bath then re-heated if necessary. Further additions of salt or alkali are often not required.

16.3.5 Problems in dyeing with reactive dyes

One of the major problems in exhaust dyeing with many reactive dyes is the rather low level of fixation, particularly when dyeing using a high liquor ratio. Often less than 70% of the original dye reacts with the fibre. This results in appreciable dye concentrations in the dyehouse effluent. This environmental problem is compounded if high salt concentrations are also present. Newer ranges of reactive dyes, particularly those with more than one reactive group that give higher fixation, have attempted to address the problem of colour in the effluent with some success. Several dye manufacturers now offer reactive dyes requiring smaller amounts of salt for exhaust dyeing. The use of less salt demands a higher degree of dye substantivity but this impedes efficient washing-off after dyeing. This is counteracted by using dyes that give good fixation.

It is possible to eliminate colour bleeding and staining of adjacent material when an article is first washed during use by aftertreating the dyeing with a cationic fixative. This type of product reacts with any residual unfixed anionic dye, forming an organic salt of greatly increased molecular size and of lower water solubility and diffusion rate. Such cationic fixatives lack permanence on repeated washing but this is not a problem since the unfixed dye will have gradually been removed by that point. They may, however, reduce the light fastness of the dyeing and are therefore more suitable for treatment of deep shades. Such an aftertreatment is not a remedy for inefficient washing-off of unfixed dye. If the amount of unfixed dye remaining in the goods is significant there is a risk of the precipitated dye–auxiliary complex rubbing off, particularly on wet abrasion.

Dyeings with a few red DCT reactive dyes on cotton are prone to increased colour bleeding because of hydrolysis of the dye–fibre bond. Unreacted chlorine atoms in the dye's reactive group may hydrolyse under warm humid storage conditions, liberating HCl. This catalyses the hydrolysis of the dye–fibre bond. The colour bleeding can be counteracted by adding a polyamine to the final rinse water that reacts with any residual reactive chlorine atoms in the bound dye.

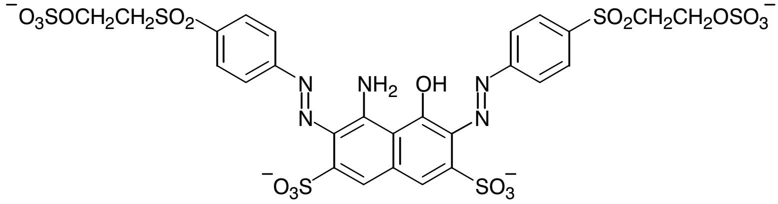
As for direct dyes, some reactive dyes may be reduced by the cellulose when dyeing at high temperatures in presence of alkali. This can lead to a significant decrease in colour strength when dyeing viscose with reactive dyes, for example. Addition of the mild oxidant *m*-nitrobenzene sulphonate usually prevents this.

There is always a risk of anionic reactive dyes being precipitated by calcium, magnesium or heavy metal ions in the water supply, or of the formation of insoluble hydroxides of these metals under the alkaline dyeing conditions. To avoid these problems, a limited addition of a polyphosphate sequestering agent may be required. EDTA should be avoided with azo copper complex dyes since demetallisation can occur with a dramatic change in hue. The copper in the stable copper phthalocyanine dyes is, however, unaffected by EDTA.

Finally, stripping reactive dyes is by no means easy. Hydrolysis of the dye–fibre bond using hot acetic acid solution, followed by good washing, may give partial stripping. Complete colour discharge is often possible by treatment with alkaline sodium hydrosulphite solution followed by hypochlorite. Before such treatments, complexed metals should be removed using EDTA.

16.4 BIFUNCTIONAL REACTIVE DYES

CI Reactive Black 5 (**3**, in Figure 16.6) has long been known to give a high degree of fixation, because with two potential vinyl sulphone reactive groups there is an increased probability of reaction with the fibre. Many of the new reactive dyes are bifunctional with identical or different reactive groupings in the dye molecule. Adding more reactive groups to a given chromophore increases the molecular weight but decreases the colour per unit weight of dye since the reactive groups



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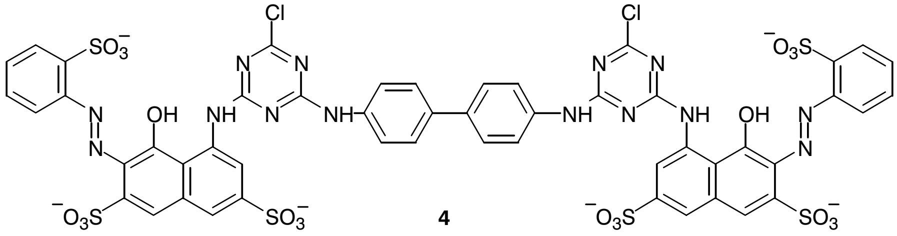

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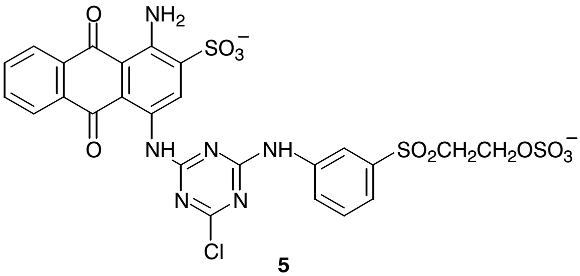

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Figure 16.6 Bifunctional reactive dyes: CI Reactive Black 5 (**3**, Remazol Black B, DyStar); Procion H-E dye (**4**); MCT-VS type (**5**) used in the Sumifix Supra dyes (Sumito).

are not part of the chromophoric system. This problem can be partly overcome, for example by linking together two DCT dyes with a suitable diamine to give a dye with two MCT groups, as in the Procion H-E dyes (**4**). This increase in molecular size usually results in an increase in substantivity that is of value for exhaust dyeing with higher liquor ratios but which can impede washing-off of unfixed dye after dyeing.

Bifunctional dyes with two reactive groups of different reactivity towards the cotton, which have different optimal fixation conditions, give a more uniform degree of fixation over a wider range of dyeing temperature and fixation pH than dyes containing two identical groups. Therefore, process control does not need to be so stringent. These types of reactive dyes give quite high fixation yields and thus less colour in the dyehouse effluent. Other important types of bifunctional reactive dyes include the MFT-VS type (Cibacron C, Ciba) and the MCT-VS type (**5**) used in the Sumifix Supra dyes (Sumito). The Kayacelon React range of dyes (Nippon Kayaku) are also bifunctional reactive dyes, having two NT reactive groups in each dye molecule.

16.5 CONTINUOUS DYEING PROCESSES FOR COTTON

16.5.1 Introduction

The first step in continuous dyeing involves padding dye solution onto full-width woven fabric. This is a very low liquor ratio dyeing method that gives the expected improved exhaustion and fixation, under appropriate conditions. The very rapid fixation (< 60 s) at high temperatures that is possible in fully continuous dyeing gives high productivity for long runs of a given colour. On the other hand, the slow dye fixation achieved during storage of a roll of impregnated fabric at room temperature (4–24 h) results in better dye diffusion and penetration into the fibres (Section 16.5.2).

There are several problems that must be considered in continuous dyeing with reactive dyes:

(1) dyes of low substantivity are desirable to avoid preferential dye absorption during padding and the initial colour tailing that it causes (Section 10.5.2). This is less of a problem with reactive dyes than with direct or sulphur dyes, which have greater molecular size and therefore higher substantivity. Tailing caused by dyes with different substantivities can result in an initial drift of the

hue. These effects can be minimised by adjusting the initial concentration and composition of the feed solution of dyes;

(2) when using pre-prepared alkaline solutions of reactive dyes, reasonable stability of the dye/alkali mixture is essential. Any premature hydrolysis of the dye's reactive group in the reservoir or pad bath will result in a loss of fixed colour. This can be controlled using a dye solution with the lowest possible pH. When the pre-mixed dye and alkali solution is not sufficiently stable, and it cannot be stored in a reservoir without an unacceptable degree of hydrolysis, metering pumps deliver known flow rates of separate neutral dye and alkali solutions, which are mixed just before entering the pad bath. A constant padding temperature must be maintained for an invariant colour yield. Having two separate padding stages solves the problem of dyes that are very susceptible to hydrolysis. In this case, a neutral solution of the reactive dye is first padded onto the goods and, after drying, the alkali solution is padded on just before the fixation stage. In some cases, a wet-on-wet two-stage padding is possible;

(3) when dyeing very deep shades, concentrated dye solutions are required. Dye solutions containing more than 50 g l^{-1} of dye may be needed if the solution is to be applied at relatively low wet pick-up to avoid migration problems during drying and excessive drying costs. For example, a 4.2% owf dyeing requires a dye solution of 70 g l^{-1} at 60% solution pick-up. The desired concentration may exceed the dye solubility, particularly if an appreciable amount of electrolyte is present. Low dye solubility can be improved by addition of relatively large amounts of urea (100 g l^{-1}). Urea helps to break up dye aggregates by hydrogen bonding to the dye molecules. It is sprinkled onto the cooled dye solution before the salt and stirred in to dissolve it;

(4) after padding with a neutral solution of reactive dyes, the fabric will often be dried. This must be done under conditions that minimise migration of unfixed dye to the fibre and yarn surfaces. Heating of the wet material must be as uniform as possible to avoid side-to-centre and back-to-face colour differences due to migration. The padding solution will usually contain salt as an anti-migrant and also a thickening agent such as sodium alginate (1 g l^{-1});

(5) in fully continuous operations, the final rinsing and soaping of goods dyed with reactive dyes are also carried out continuously. These processes take place at high fabric speeds and the goods are only in contact with the washing solutions for short periods of time. Therefore, washing-off is usually less

effective than washing in a dyeing machine where longer washing times and fresh baths are more easily arranged. The usual eight box washing range allows three dilution rinses, 2–3 soapings and 2–3 final rinses. For initial rinsing, static baths, into which no water flows, are more economical. The concentration of salts accumulating in the static bath must not become so high that soaping efficiency falls because the unfixed dye is too substantive. It is common to have a counter-current flow of water through each short series of boxes before the last bath overflows to the drain. The flow rate of water must provide the required degree of dilution and of unfixed dye removal so that the final fabric has acceptable fastness properties.

16.5.2 Pad–batch dyeing

Pad–batch dyeing involves padding the fabric with a pre-mixed alkaline solution of the reactive dyes and then winding up the impregnated fabric on a suitable roller. Fixation occurs during storage of the batched fabric at ambient temperature. The dye and alkali solutions are usually mixed just before padding using metering pumps to maintain the correct ratio. A 4:1 dye-to-alkali solution volume ratio is very common. During storage, the roller may be continuously rotated at low speed to avoid drainage of the internal liquid within the batch.

Obviously, the dyes must have adequate reactivity under the batching conditions to give good fixation within about 24 h. The more reactive dyes give effective fixation within 2–6 h. To avoid evaporation from the exposed surfaces and edges of the roll, the fabric is stitched to a somewhat wider end-cloth that is padded and finally wrapped around the entire wet roll before it is covered with a plastic film. When padding on solutions with relatively high pH values, which are necessary to promote fixation of less reactive dyes, there is always a risk of carbon dioxide absorption on the selvages of the material even when these have been accurately wound edge-on-edge. This decreases the solution pH since hydroxide ion is converted into carbonate ion. The rate of fixation is then lowered. The effect of this only becomes apparent after the final washing when the selvages appear paler than the rest of the material. In pad–batch dyeing with Remazol dyes (DyStar), the buffering action of sodium metasilicate added to the NaOH solution is claimed to virtually eliminate the problem of paler selvages from carbon dioxide absorption.

After storing, the batch of material must be thoroughly washed to remove unfixed dye and chemicals. If the fabric is wound on a perforated beam, this can be carried out using a beam dyeing machine. Alternatively, other types of batch dyeing machine or a continuous washing range can be used.

This semi-continuous pad–batch process offers many advantages and is now widely used in place of jig dyeing. Provided that space is available for storage of the fabric batches, the energy requirements for dyeing are minimal and the process is more economic than batch dyeing for lots in the 1000–10 000 m range. The fabric also often has a better handle and surface appearance because it is not continuously circulating around in a winch or jet dyeing machine. The relatively slow fixation process results in good dye penetration into the fibres.

16.5.3 Pad–heat dyeing

The pad–dry process is only suitable for reactive dyes with fairly high reactivity. For dyes of lower reactivity, the dried fabric must be baked to promote further fixation. In pad–dry dyeing, the fabric is first padded with a dye solution containing sodium bicarbonate. During drying, bicarbonate is converted into carbonate, which gives a higher pH and more effective fixation (Scheme 16.4). The dye solution also contains a high concentration of urea (100 g l^{-1}). This helps the cotton fibres retain water during drying, possibly provides a fluid medium for dye diffusion in the fibres at low water contents, and increases dye solubility. Unfortunately, all this urea is removed on washing after fixation and poses a pollution problem. Urea is a source of nitrogen nutrients for algal growth.

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

Scheme 16.4

In the pad–dry process, typically with the reactive DCT dyes, the drying rate is fairly low and the cotton retains at least 18% water. If the fabric is fully dried, the reaction ceases so the drying time must be longer than that for effective reaction with the cotton. Typical conditions are 2–5 min at 105 °C in a hot flue or on heated cylinders at 105 °C. The fabric temperature will not exceed 70 °C. The initial drying cylinders may be much cooler to avoid excessively high initial evaporation rates and migration.

The pad–dry–bake process is suitable for less reactive dyes such as MCT dyes. Today, this type of process is used mainly in combination with the application of disperse dyes to cotton/polyester materials using the Thermosol process (Section 15.7.6). Baking temperatures of 200–220 °C for 1 min are typical but may be lower (150–170 °C) if only cotton is being dyed. When dyeing deep shades, the degree of fixation is usually lower. The fabric tends to yellow at high baking temperatures and this can influence the hue of pale shades. The most popular variant of this process for dyeing cotton/polyester fabrics is the neutral thermofix method. For this a solution of reactive and disperse dyes containing sodium bicarbonate is padded onto the cotton/polyester using dicyanodiamide, $H_2N{-}C(=NH){-}NH{-}CN$, in place of urea. Both fibres are dyed simultaneously by heating at around 200 °C for 1 min. As in all reactive dyeing processes, the final step is a thorough washing to remove unfixed dyes.

16.5.4 Pad–steam dyeing

In this process, the goods are padded with a solution containing the reactive dyes, salt and the appropriate alkali. Again only selected dyes are suitable and the manufacturer's recommendations should be followed. The hot humid conditions during steaming tend to cause excessive hydrolysis of the reactive group and thus lower the colour yield. In dyeing terry towelling and other pile fabrics, a two-stage wet-on-wet padding version of this process is used to avoid an intermediate drying step. The towelling is first padded with a neutral solution of the reactive dyes, and then with a solution of the alkali prior to steaming. In wet-on-wet padding, the pick-up of the second solution should be sufficiently high to give good fixation, and colour bleeding into the second pad bath must not be excessive.

16.5.5 Pad–dry–pad–steam dyeing

This is the predominant fully continuous reactive dyeing process. The fabric is padded with a neutral solution of the reactive dyes, dried and then padded with the alkali solution containing salt before steaming. The dye solution is quite stable, because there is no alkali present in the dyebath. Some salt or anti-migrant agent helps to minimise migration of the dyes to the yarn surfaces during the initial stages of drying. The intermediate drying ensures a uniform and high pick-up of the alkaline salt solution and minimises bleeding of dye into the chemical pad. After drying, the fabric must be cooled on cold cylinders to avoid heating the chemical pad solution. Since sodium carbonate is difficult to dissolve in salt solution, sodium hydroxide is the preferred alkali. There are a number of variations of this type of process and it is also incorporated into the continuous dyeing of cotton/polyester materials using disperse and reactive dyes (Sections 10.5.3 and 23.7.3)

16.5.6 Application of reactive dyes and finishing chemicals

Reactive dyes may be applied to undyed cellulosic materials at the same time as the usual crease-resist and durable press resin finishes, thus combining dyeing and finishing into one step. During curing, when the methylolamino groups ($–NHCH_2OH$) of the polyfunctional finishing chemicals react with hydroxyl groups in the cellulose (Section 25.3.1), the dye reacts with free amino groups in these agents rather than with the fibre. Since the dye is fixed to the finishing agent, the fastness properties of the final dyeing depend on the permanence of the finish.

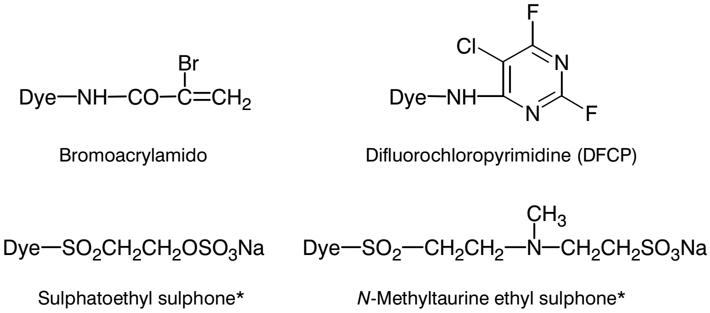
16.6 REACTIVE DYES FOR WOOL [2]

16.6.1 Introduction

The somewhat late development of fibre-reactive dyes was partly caused by a lack of appreciation of the considerable reactivity of fibres made of cellulose or proteins. A number of dyes developed for wool with 2-sulphatoethylsulphone or chloroacetylamino groups were not immediately recognised as reactive dyes. In fact, the development of reactive dyes really started with the introduction of the Procion dyes for cotton by ICI in 1955.

Despite the many possible reactive groups in dyes capable of covalent bond formation with nucleophilic groups in wool, only a limited number of types of reactive dye have been commercially successful. Figure 16.7 shows the major types of reactive groups. The dye chromophores are essentially those used for cotton reactive dyes.

The most important reactive groups in wool are all nucleophilic and are found mainly in the side-chains of amino acid residues. They are, in order of decreasing reactivity, thiol (the –SH of cysteine), amino (–NH– and $–NH_2$ of say histidine and lysine) and hydroxyl groups (–OH of serine or tyrosine). Difluorochloropyrimidines undergo aromatic nucleophilic substitution of one or both fluorine atoms, the fluorine between the two nitrogen atoms being the most reactive. Bromoacrylamido groups are stable in boiling water at pH 7 and react by



(*give vinyl sulphone)

Figure 16.7 Types of reactive dyes for wool

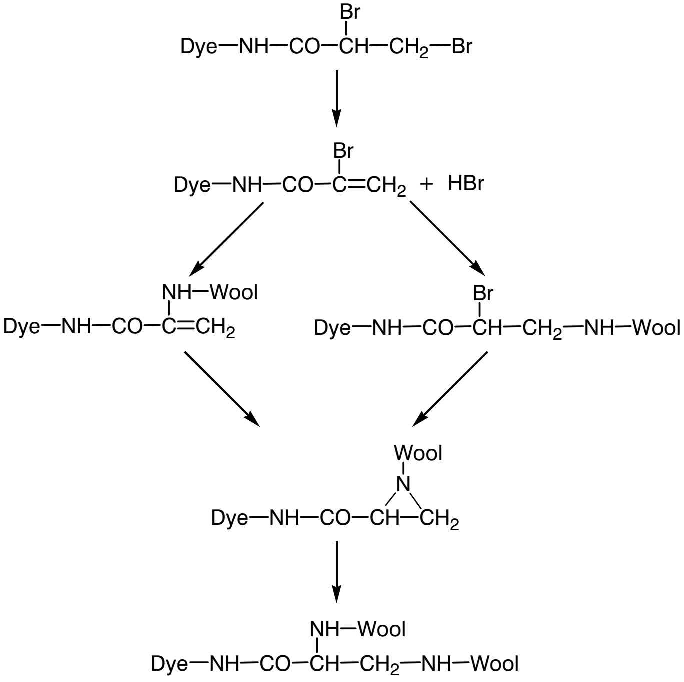


Figure 16.8 Reactions of bromoacrylamido reactive dyes with wool

$$\text{Dye—NHCOCH}_2\text{Cl} + \text{Wool—SH} \longrightarrow \text{Wool—S—CH}_2\text{CONH—Dye} + \text{HCl}$$

Scheme 16.5

both nucleophilic addition to the double bond and nucleophilic substitution of the bromine atom (Figure 16.8). They can form a three-membered aziridine ring that can react further with the protein resulting in a new crosslink. The actual dyes are probably dibromopropionamides, which eliminate HBr on dissolving in hot water. Methyltaurine-ethylsulphones and 2-sulphatoethylsulphones form the vinyl sulphone reactive group relatively slowly at pH 5–6 (1 h at the boil). This allows some levelling during dyeing before the vinyl sulphone dye reacts with the wool and becomes immobilised. This is useful in hank and winch dyeing where the liquor/goods interchange is less favourable. In fact, all commercial reactive dyes for wool have absorption rates that are greater than the rate of reaction with the fibre to allow some migration. Chloroacetylamino groups ($-NHCOCH_2Cl$) react by an S_N2 mechanism (Scheme 16.5).

Wool reactive dyes are applied like acid dyes in weakly acidic solution. The degree of exhaustion and fixation are usually very high and clearing of unfixed dye from the goods may only be needed for deep shades. Reactive dyes for wool tend to be unlevel dyeing and are prone to give skittery dyeings. They are used more on loose fibre and slubbing than on piece goods, where they accentuate fibre non-uniformity and poor, uneven fabric preparation. A number of amphoteric or weakly cationic auxiliary products are available to assist level dyeing. Despite their good light fastness and very good washing fastness, they are still not widely used, partly because of their high cost. Red to maroon shades are very popular but there are no black reactive dyes available that can match the chrome blacks on wool.

16.6.2 Batch dyeing of wool with reactive dyes

Reactive dyes are usually applied to wool at pH 5–6 using ammonium salts, and acetic acid as required. At higher pH values, exhaustion is too low, and at lower values rapid dye uptake gives unlevel dyeings. Slightly higher pH values are used for dyeing paler shades (pH 5.5–6.0) and lower values (pH 5.0–5.5) for deep shades. Reactive dyes often give quite good exhaustion at temperatures below the boil but the dyeing temperature will eventually be raised to 100 °C to ensure that reaction with the wool is as complete as possible. Some procedures recommend a holding stage at an intermediate temperature of 65–70 °C for 15–20 min to allow the dye to migrate before it reacts with the wool.

Because of their tendency to give unlevel, skittery dyeings, reactive dyes are usually applied to wool in the presence of proprietary levelling agents. These are often amphoteric, having both cationic and anionic groups in the molecule. In contrast to most levelling agents, which decrease the dyeing rate, the auxiliary products for dyeing wool with reactive dyes accelerate dyeing. The anionic dye complexes with the cationic site in the auxiliary product but the remaining anionic site provides substantivity for the wool surface. The bulky dye–auxiliary complex exhausts well onto the fibre surface at relatively low temperature, better than the dye alone, but cannot penetrate into the fibres. The complex breaks down as the dyeing temperature increases so that the smaller liberated dye molecules can then absorb into the wool. The use of such products avoids unlevel, skittery dyeings and provides better compatibility of dye mixtures.

Deeply dyed goods must be aftertreated to remove unfixed dye so as to give the best wet fastness. This is particularly important to ensure that there is no staining of adjacent undyed material during washing. After dyeing, the material can be washed at 80 °C for about 15 min using a dilute ammonia solution at pH 8.0–8.5, and then rinsed in water with a little acetic acid. To avoid any alkali damage to the wool, washing can be done with hexamine (hexamethylenetetramine from formaldehyde and ammonia) at pH 6.5, or with sodium bicarbonate. Certain proprietary chemicals can be added to the dyebath on completion of dyeing and their hydrolysis increases the bath pH to around 7. For example, hydrolysis of sodium trichloroacetate gives chloroform, carbon dioxide, both of which are volatile, and sodium hydroxide (Scheme 16.6). The actual colour removed may consist of unreacted dye, hydrolysed dye and products of the reaction of the dye with soluble wool hydrolysis products such as ammonia and hydrogen sulphide or amino acids.

$$\mathrm{CCl_3{-}CO_2Na} + \mathrm{H_2O} \longrightarrow \mathrm{HCCl_3} + \mathrm{CO_2} + \mathrm{NaOH}$$

Scheme 16.6

Shrink-proof wool, which has been treated with resins in the Hercosett process, remains cationic on the surface and gives rapid uptake of reactive dyes. The usual auxiliary levelling agents may be less effective in this case. The deposited resin protects the wool from damage and the best fastness results for deep shades are obtained by dyeing at 110 °C for 30 min.

Wool dyed in deep shades with reactive dyes is better protected from damage during dyeing. A number of explanations for this have been proposed. These involve protein chain crosslinking, reaction with thiol groups that interferes with the reformation of disulphide links, and reaction with non-keratinous proteins in the cell membrane complex and endocuticle.

16.6.3 Semi-continuous methods for reactive dyes on wool

Reactive dyes can be applied to both wool cloth and tops by padding followed by batching for 24–72 h. A thickener is added to the pad liquor to give a high solution pick-up. High concentrations of urea are used and the solution also contains sodium metabisulphite. Urea breaks up dye aggregates and sodium metabisulphite reduces cystine crosslinks in the wool, generating more reactive thiol groups. This promotes higher and more uniform fixation. The combination of urea and metabisulphite ($Na_2S_2O_5$, gives $NaHSO_3$ on hydrolysis) in the padding solution results in greater fibre swelling and better dye penetration. Dyes with activated double bonds react with bisulphite by nucleophilic addition and are converted into non-reactive forms so the pad solutions are not particularly stable. The pad–batch method can be used with reactive dyes normally applied to cotton, such as Procion MX and Drimarene K dyes. The dyed goods are then treated with dilute ammonia, rinsed and neutralised with acetic acid to remove unfixed dye. This type of process is very economical and reduces fibre damage.

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CHAPTER 17

Vat dyes

17.1 INTRODUCTION

This chapter discusses vat, indigo and sulphur dyes together because their use in dyeing involves the same principles. Vat dyes are one of the oldest types of dye. Vat dyes in particular give dyeings on cellulosic fibres with the best overall fastness properties. Because of the popularity of blue jeans, Indigo is still one of the most important of all dyes in present use. Natural Indigo was obtained by extraction from leaves, by fermentation in wooden vats, the origin of the term 'vatting'. Today, Indigo is synthesised from manufactured intermediates. Its application involves reduction to the water-soluble leuco compound, dyeing the cotton and re-oxidation of the leuco dye in the fibres to the insoluble pigment, the three basics steps involved in vat dyeing (Figure 1.4).

Vat dyes are water-insoluble pigments. They are called dyes because chemical reduction in alkaline solution converts the pigment into a water-soluble leuco form with substantivity for cotton. The vat pigment and the leuco compound often have quite different colours – blue and pale yellow in the case of Indigo – so the progress of the reduction is often easy to observe. After dyeing with the leuco compound, the pigment is regenerated in the dyed cotton by oxidation. The overall process therefore involves three key steps:

(1) reduction of the pigment to the soluble leuco compound, a process called vatting;
(2) absorption of the leuco compound by the cotton during dyeing;
(3) oxidation of the absorbed leuco compound in the cotton, reforming the insoluble pigment inside the fibres.

The use of strongly alkaline solutions (pH 12–14) for vatting and dyeing limits the use of most vat dyes to cellulosic fibres.

17.2 CHEMICAL CONSTITUTION OF QUINONE VAT DYES

In the case of Indigo, vatting involves reduction of a pair of conjugated carbonyl groups (Figure 1.4). For most vat dyes, these carbonyl groups are present in an anthraquinone or polycyclic quinone. The parent quinone is an insoluble pigment (**1**, in Figure 17.1). The leuco compound is the sodium salt of the diphenol or hydroquinone formed by reduction in NaOH solution (**2**). It is reasonably soluble in water, substantive to cotton and easy to oxidise back to the red pigment. Reduction is carried out in strongly alkaline solution to avoid formation of the vat acid (**3**). This is the free diphenol formed by protonation of the anionic leuco derivative. The vat acid is insoluble in water, has no substantivity for cotton and is more difficult to oxidise.

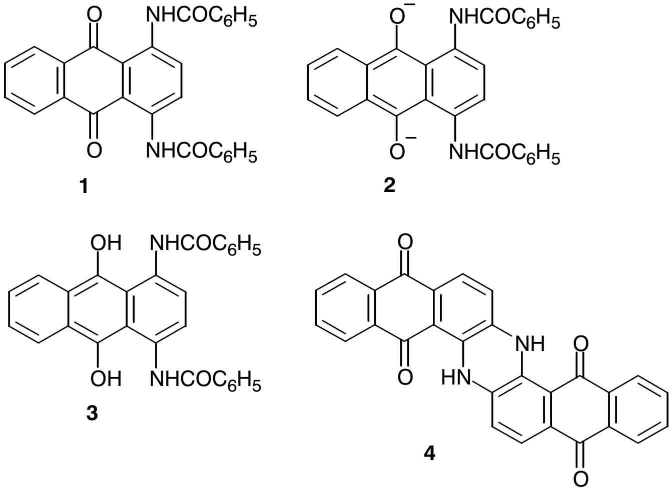


Figure 17.1 CI Vat Red 42 (**1**); leuco compound formed by reduction (**2**); vat acid formed by protonation of the anionic leuco derivative (**3**); CI Vat Blue 4 (**4**)

Quinone vat dyes are usually either anthraquinone derivatives (**1**) or polycyclic quinones. Indanthrone (**4**), the first quinone vat dye, was discovered by accident during attempts to make an Indigo-type derivative from 2-aminoanthraquinone. The structures of most vat dyes are often quite complex and have no ionic groups. Many of the polycyclic derivatives have no attached substituents, but a few have halogen, hydroxyl, methoxyl or amide groups. The more complex dyes may have several reducible quinone groups (Figure 17.2).

The molecular structure of a vat dye influences the water solubility, substantivity and rate of diffusion into the cotton of the leuco compound used in dyeing. A classification of quinone vat dyes according to dyeing characteristics is more useful for our purpose and will be given later in this chapter.

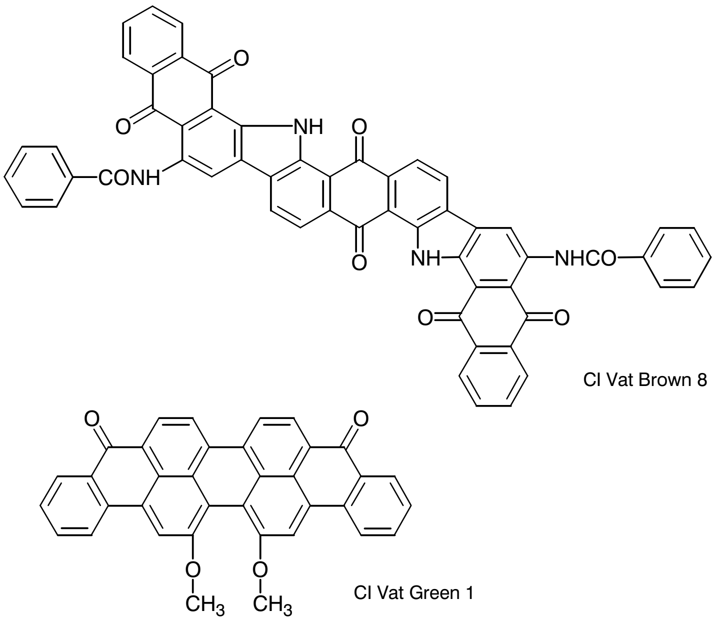


Figure 17.2 Molecular structures of complex anthraquinone and polycyclic vat dyes

17.3 THE REDUCTION OF QUINONE VAT DYES

17.3.1 Vat dye dispersions

Quinone vat dyes are available as fine powders or grains, and as liquid dispersions or pastes. The insoluble pigment is extensively milled with dispersants such as sodium lignosulphonates to produce very small particles (Section 15.3). Typically, at least 50% of the particles will have diameters less than 1 μm. All forms must disperse readily in water and any aggregates of particles must easily break up to give a fine, stable dispersion. The rate of reduction to the leuco form is usually faster, the finer the pigment dispersion.

Solid forms contain much dispersing agent and more may be added to the dyebath to keep any unreduced dye in suspension. Addition of sodium hydrosulphite (dithionite) ($Na_2S_2O_4$) to the alkaline aqueous dispersion of the vat dye brings about rapid reduction. In pigmentation dyeing methods, the fine pigment particles are uniformly deposited in the goods by padding or liquor circulation before reduction occurs. Very fine dispersions are needed for these pigmentation processes and the proportion of fine particles is higher than for vat pigments in the traditional vatting process. Dye powders for pigmentation dyeing have higher dispersant content. Pastes and liquid forms are useful for printing and continuous dyeing. They will usually have less dispersant but contain appreciable amounts of water. Some ranges of dyes are deliberate mixtures of vat and disperse dyes for dyeing cotton/polyester blends.

17.3.2 Reducing vat dyes with hydros

Reduction of quinones is not easy and vatting requires a strong reducing agent. The dihydrate of sodium dithionite, or hydrosulphite, $Na_2S_2O_4.2H_2O$, is used almost exclusively and goes by the common name of 'hydros'. Vatting is carried out under strongly alkaline conditions for a number of reasons:

(1) the reduction of the quinone (QO_2) with hydros to give the leuco dye (QO_2^{2-}), and the oxidation of the hydros by oxygen, consume alkali (Scheme 17.1);

(2) it is important that the insoluble vat acid does not precipitate;

(3) hydros is unstable in solution, particularly under acidic or neutral conditions and at higher temperatures. Its decomposition forms thiosulphate and bisulphate. This decomposition reaction consumes hydroxide ion and it is faster as the solution becomes more acidic (Scheme 17.2).

$$QO_2 + Na_2S_2O_4 + 4NaOH \rightleftharpoons QO_2^{2-} + 2Na^+ + 2Na_2SO_3 + 2H_2O$$

$$Na_2S_2O_4 + 2NaOH + O_2 \rightleftharpoons Na_2SO_3 + Na_2SO_4 + H_2O$$

Scheme 17.1

$$2Na_2S_2O_4 + 2NaOH \longrightarrow Na_2S_2O_3 + 2Na_2SO_3 + H_2O$$

Scheme 17.2

The decomposition of hydros is exothermic. Decomposition of solid $Na_2S_2O_4.2H_2O$ can lead to spontaneous ignition. Cool, dry conditions are therefore necessary for storage. Decomposition of hydros occurs rapidly in acidic solution. Alkaline hydros solutions are more stable provided oxygen is absent.

Because hydros reacts readily with oxygen (Scheme 17.1), the material being dyed with the leuco dye should not be over-exposed to air. Oxidation of the excess hydros can lead to subsequent oxidation of the leuco dye and precipitation of the quinone, giving uneven surface deposits of pigment on the goods. A large excess of hydros in the bath is usual. The amount used depends on the dyes and the type of machine. The suppliers give suitable recommendations for their dyes. Other more stable reducing agents, such as sodium sulphoxylate-formaldehyde ($HOCH_2SO_2Na$), are used in printing with vat dyes to ensure stability of the pastes. Steaming of the printed material activates this reducing agent and the vat dye in the print paste is reduced (Scheme 23.3). Sodium sulphoxylate-formaldehyde is a poor reducing agent at 25 °C and is more stable than hydros. Other reducing agents such as thiourea dioxide (Scheme 23.3) and glucose are now being suggested as more environmentally friendly alternatives to hydros.

17.3.3 Vatting

Traditional vatting involves adding hydros to a fine, relatively concentrated aqueous dispersion of the vat dye pigment containing NaOH. The vatting temperature is often higher than the subsequent dyeing temperature. This gives rapid reduction. The concentrated solution of the leuco form is then diluted by adding it to water in the dyebath. The bath water also contains NaOH and some hydros to avoid any oxidation from dissolved atmospheric oxygen. Vatting may also be carried out directly in the dyebath if the dye is readily reduced.

Dyeing takes place at temperatures lower than the vatting temperature to avoid decomposition of the hydros. This also decreases the risk of over-reduction of polyquinone dyes such as Indanthrone. Over-reduction is the reduction of more than one pair of conjugated carbonyl groups in a polyquinone and often results in poor colour yields and off-shade dyeings. Reduction inhibitors, such as sodium nitrite or glucose, prevent over-reduction during vatting. Anthraquinone and polycyclic vat dyes give leuco solutions with intense colours, often very different from those of the original pigment dispersion. The vat dye flavanthrone is a yellow pigment that produces a deep blue vat. It is often used in paper strips for the detection of excess hydros.

Vatting conditions for quinone vat dyes vary widely. Three main types of vatting process are used depending upon the dyes being used. These involve:

(1) a concentrated NaOH solution and a high vatting temperature (60 °C);

(2) a moderate concentration of NaOH and a lower vatting temperature (50 °C);
(3) a low concentration of NaOH and a low vatting temperature (30–40 °C).

17.3.4 Redox potentials and rate of vatting

Dyes that are easy to reduce are more difficult to oxidise, and vice versa. The standard redox potential ($E°$) gives a measure of the ease of reduction at a given pH. In strongly alkaline solution, the redox potential E is given by

$$E = E° + \frac{RT}{2F} \ln\left(\frac{a_{\text{ox}}}{a_{\text{red}}}\right) \tag{1}$$

where R is the gas constant, T the absolute temperature, F the Faraday constant, and a_{ox} and a_{red} are the activities of the oxidised and reduced forms of the vat dye. The value of $E°$ is related to the standard free energy change for the reduction process.

$$\begin{gathered} \text{ox} + 2\text{e}^- \rightleftharpoons \text{red}^{2-} \\ -\Delta G° = 2E°F = RT\ \ln(K) \end{gathered} \tag{2}$$

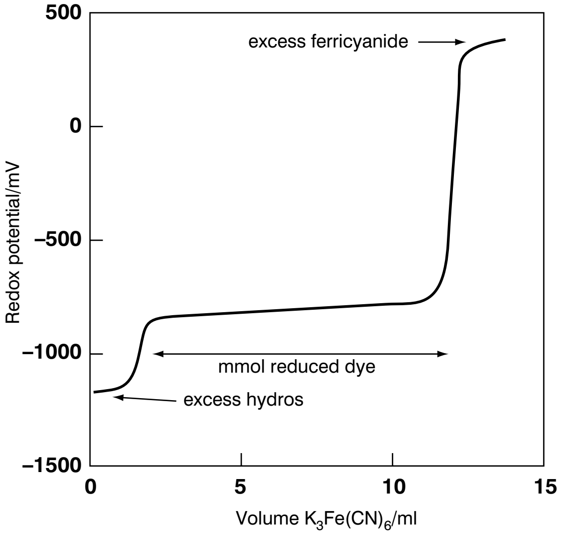


Figure 17.3 Potentiometric titration curve for oxidation of a leuco vat dye showing hydros, ferricyanide and dye potentials and total dye content

Anthraquinone vat dyes have large negative standard redox potentials, giving unfavourable positive values of ΔG°, and therefore their reduction requires strong reducing agents. Conversely, the leuco compound in alkaline solution is readily oxidised. The potentiometric titration of the leuco compound in solution with an oxidising agent is complicated by the precipitation of the insoluble quinone pigment, even in the first stages of the titration. This usually results in unstable potentials and the usual form of the titration curve is not followed. Complete oxidation of the leuco form can, however, usually be detected and the titration is useful for analysis of the actual dye content of vat dye samples (Figure 17.3). The titration is usually performed using potassium ferricyanide solution as oxidising agent. The reaction involved is:

$$QO_2^{2-} + 2Fe(CN)_6^{3-} \rightleftharpoons QO_2 + 2Fe(CN)_6^{4-} \qquad (3)$$

The number of moles of leuco dye oxidised is given by:

$$\text{mmol dye} = 0.5 \times V(\text{ml}) \times \text{M}(\text{mmol ml}^{-1}) \qquad (4)$$

where V is the volume of ferricyanide solution for quantitative oxidation and M its molarity.

A typical vat dye has a redox potential around –0.80 V with respect to a standard hydrogen electrode. Alkaline hydros solution has a potential of about −1.10 V. The standard potential for the reduction reaction is calculated as follows:

$$\begin{aligned} QO_2(\text{ox}) + 2e^- &\rightleftharpoons QO_2^{2-}(\text{red}) \quad E^o = -0.80\ \text{V} \\ 2SO_3^{2-} + 4H^+ + 2e^- &\rightleftharpoons S_2O_4^{2-} + 2H_2O \quad E^o = -1.10\ \text{V} \end{aligned} \qquad (5)$$

Combination of the first with the reverse of the second equation gives:

$$QO_2 + S_2O_4^{2-} + 2H_2O \rightleftharpoons QO_2^{2-} + 2SO_3^{2-} + 4H^+$$

which is essentially the same as the first equation in Scheme 17.1.

$$E^\circ = -0.80 - (-1.10) = +0.30\,\text{V} \qquad (6)$$

$$\log(K) = \frac{2E^\circ F}{2.303RT} = \frac{2 \times 0.30 \times 96485}{2.303 \times 8.314 \times 298} \approx 10^{10}$$

Obviously, such a large equilibrium constant for the reduction means that hydros solution is a sufficiently powerful reducing agent to completely reduce the vat dye pigment to the leuco form. Similar considerations apply to the oxidation of the leuco derivative. Any oxidising agent with a redox potential below about –0.60 V will give quantitative oxidation back to the quinone form of the dye.

$$\begin{aligned} QO_2(\mathrm{ox}) + 2e^- &\rightleftharpoons QO_2^{2-}\,(\mathrm{red}) \quad E^\circ = -0.80\ \mathrm{V} \\ O_2 + H_2O + 2e^- &\rightleftharpoons HO_2^- + HO^- \quad E^\circ = -0.10\ \mathrm{V} \end{aligned} \tag{7}$$

Thus, combination of the second with the reverse of the first equation gives

$$\begin{gathered} QO_2^{2-} + O_2 + H_2O \rightleftharpoons QO_2 + HO_2^- + HO^- \\ E^\circ = -0.10 - (-0.80) = +\,0.70\ \mathrm{V} \end{gathered} \tag{8}$$

For oxidation of the leuco derivative with oxygen, $E^\circ = +0.70$ V and the equilibrium constant is enormous.

Standard redox potentials are thermodynamic values related to the position of equilibrium and give no information about reaction rates. Hydros is a very strong reducing agent, more effective at high pH and at higher concentration. Its potential is unstable but negative enough that it will reduce almost all vat dyes, but not necessarily rapidly. Indigo dyes, for example, have less negative standard potentials than anthraquinone vat dyes but reduce more slowly. Attempts to control the amount of hydros needed in vatting and during dyeing, based on redox potential measurements of the dyebath solution, have not been particularly successful. It is difficult to interpret the recorded potentials in a way that allows calculation of the amount of excess hydros and to keep the required platinum electrodes in good condition.

The reducing action of hydros is complex. The dithionite ion is a good reducing agent but much of its reducing power depends upon formation of the dithionite radical formed by breaking the weak bond between the two sulphur atoms in dithionite (Scheme 17.3). The kinetics of the reduction process depend on the temperature and concentrations of chemicals in solution, the rate increasing with increase in the temperature and the concentration of hydros. The rate of reduction of a vat pigment is, however, complicated by the heterogeneous nature of the system and depends upon the size distribution and habit of the crystals in dispersion. The crystalline form affects the rate of vatting more than the particle size but, in general, the rate of reduction is higher for finer particles. The effects of these physical parameters are far less significant than the differences between dyes of different structures. Vatting rates are fairly easy to measure since the solution of the leuco compound usually has a colour quite different from the quinone pigment. Times of half reduction (the time required to achieve 50% reduction of the pigment dispersion under given conditions) vary by a factor of over 600.

$$^{-}O_2S{-}SO_2^{-} \rightleftharpoons 2SO_2^{\bullet -}$$

Scheme 17.3

Rates of vat dye reduction show no correlation with their redox potentials. Redox potential values allow calculation of the extent of reduction at equilibrium with a given reducing agent of known concentration and potential; they do not give the rate at which equilibrium is reached. A rapid rate of reduction of the vat pigment is much more important in continuous dyeing and printing where reduction and adsorption are concurrent. In printing, the rate of reduction must be higher than the rate of decomposition of the reducing agent under the given steaming conditions. Whenever possible, dyes that reduce slowly are vatted at higher temperature unless decomposition is a problem.

17.4 THE SUBSTANTIVITY AND DYEING CHARACTERISTICS OF VAT DYES FOR CELLULOSIC FIBRES

17.4.1 Basic steps in the dyeing process

The dyeing of cellulosic materials with quinone vat dyes follows a four-step sequence:

(1) preparation of the vat containing the leuco forms of the dyes;
(2) dyeing of the material, in which the fibres absorb the water-soluble leuco compound;
(3) oxidation of the absorbed leuco compound back to the parent pigment inside the fibres;
(4) soaping of the dyed material to remove pigment loosely adhering to the fibre surfaces and to develop the true shade and fastness properties.

17.4.2 Classification of vat dyes

For quinone vat dyes, there is no single classification according to dyeing properties as is the case for the direct dyes. The German Interessen Gemeinschaft für Farbenindustrie (IG) developed one popular classification for their Indanthrene range of vat dyes based on leuco compound substantivity and the required dyeing conditions. There were three main types:

(1) the IN (indanthrene normal) group of dyes require the use of concentrated NaOH and high vatting (60 °C) and dyeing temperatures (60 °C). No salt is added to the dyebath because of the high substantivity of the leuco dyes for cotton;

(2) the IW (indanthrene warm) group of dyes require only moderate amounts of NaOH and lower vatting (50 °C) and dyeing temperatures (50 °C). The leuco forms of these dyes have moderate substantivity for cotton and some addition of salt is needed during dyeing to aid exhaustion;

(3) the IK group of dyes only need a low concentration of NaOH with low vatting (40 °C) and dyeing temperatures (20 °C). These dyes have low substantivity for cotton and need considerable salt for good dyebath exhaustion. Some have amide groups that would be hydrolysed under the vatting and dyeing conditions used for IN and IW dyes.

There are special processes for some black vat dyes that require an oxidative aftertreatment to develop the full black colour. Table 17.1 compares the characteristics of these three types of vat dye. The required concentrations of hydros, caustic soda and salt increase with increasing amounts of dye in the bath and with increasing liquor ratio.

Table 17.1 Characteristics of the three main types of vat dye

	Vat dye type		
Conditions	IN	IW	IK
NaOH concentration (g l^{-1})	4.5–7.5	2.0–4.0	1.5–2.5
NaCl concentration (g l^{-1})	0	5–25	10–40
Dyeing temperature (°C)	50–60	45–50	20–25
Vatting temperature (°C)	50–60	45–50	40

There are various other classifications of vat dyeing methods. The SDC recommend tests to determine the best dyeing method [1]. In this, the colour strengths of dyeings produced under different dyeing conditions are compared with those of standard dyeings using a grey scale. This test applies only to anthraquinone dyes. There are also SDC tests for determining the strike, migration and levelling characteristics of vat dyes. Different companies have different classification systems for their vat dyes. Because vatting and dyeing conditions vary from one dye to another, the suppliers' recommendations should be consulted.

17.4.3 The high substantivity of leuco vat dyes

The origin of the substantivity of leuco vat dyes for cotton is far from clear. Hydrogen bonds between cellulose hydroxyl groups and phenolate ion groups, or amino or amide substituents, in the leuco dye may be involved in dye–fibre binding. The substantivity of the leuco dye is very dependent on the position of the phenolate ion groups and on the actual molecular structure. Substantivity tends to be greater the larger the surface area of the leuco dye molecule and van der Waals interactions between the dye and fibre are important. Molecules of leuco vat dyes tend to be large and, although coplanarity of the structure is essential, the structures are often not long and linear as for direct dyes. Although the planar molecular structures of leuco vat dyes should promote aggregation, there is not much evidence of this in dyeing solutions.

In the dyeing process, the influence of salt addition and increasing dyeing temperature are similar to the effects found in dyeing cotton with direct dyes. Unlike direct dyes, however, dyeing with many leuco vat dyes is very rapid at relatively low temperatures and usually gives high exhaustion at equilibrium. The ability to control the dyebath exhaustion by salt addition is very limited since the bath initially contains a high concentration of sodium ions from the added hydros and caustic soda. Because of this, many dyes have a rapid strike. The dyebath may be 80–90% exhausted within 10 minutes. Because there is little diffusion into the fibres within such a short period, there is a strong tendency for cotton yarns and fibres to be ring dyed in the early stages of dyeing. Diffusion only becomes important well after the time of half dyeing. The high strike must be controlled to avoid unlevel dyeing since the low dyeing temperatures do not favour migration. The behaviour of the leuco dyes is assessed by the usual migration and strike tests in comparison with the behaviour of standard dyes [1]. The dyeing methods recommended correspond to the IN, IW and IK methods described in Section 17.4.2.

The rate of diffusion of a typical leuco vat dye into cotton is about half that of a direct dye at the same temperature. The high rate of dyeing of leuco vat dyes is therefore a consequence of their high substantivity for cellulose. Since the standard affinities of leuco vat dyes are no higher than those of direct dyes, the high substantivity and rate of dyeing are caused more by the high electrolyte content of the dyebath than by high inherent affinity.

The initial strike can be retarded using polyethylene oxide complexing agents. The initially formed dye–auxiliary complex presumably slowly breaks down to gradually liberate free leuco dye, thus controlling the initial rate of adsorption. Both non-ionic and cationic retardants are used but these decrease the exhaustion. They can also be used for levelling of uneven dyeings. Such dyeing auxiliaries should be added to the dyebath after vatting. The dye manufacturer's recommendations should be consulted since these agents are often dye-specific. Similar chemicals can be used for stripping faulty dyeings. This is not easy because of the high substantivity of the leuco vat dyes and the stripping auxiliaries used form much more stable complexes with the leuco dyes than those obtained from levelling agents.

17.5 DYEING COTTON WITH LEUCO VAT DYES

17.5.1 Preparation

As always, good preparation of the goods is essential to avoid a non-uniform distribution of residual impurities that might hinder level dyeing or that might interact with the dyes. Water quality is important since the calcium and magnesium salts of some leuco dyes may precipitate if hard water is used. The use of sequestrants or protective colloids is often recommended.

17.5.2 Dyeing conditions

Quinone vat dyes are used on all forms of cellulosic materials. The vat is usually pre-prepared and added to the dyebath containing the goods, possibly in successive portions. Vat dyes of high substantivity are often used for dyeing deeper shades where the effect of poor levelling is less visible. They usually follow a Freundlich adsorption isotherm (Section 11.1.1) so that using more dye gives deeper shades, but with diminishing returns. The dyeing temperature may be increased to promote migration, if the dye is stable. This gives better penetration into tightly constructed materials. Subsequently cooling the dyebath promotes better exhaustion. Any required salt may be added in portions towards the end of the process for dyes of lower substantivity.

The liquor ratio is usually in the range from 10:1 to 20:1. The actual amounts of caustic soda and hydros required for vatting, and for addition to the dyebath, depend on many factors, such as the dyeing temperature and time, and particularly on the degree of exposure to air during dyeing. The latter is mainly a characteristic of the particular dyeing machine used. As in dyeing cellulosic fibres with some direct dyes, the rate of dyeing with leuco vat dyes is higher at higher temperature, lower liquor ratio and lower dye concentration. It is not much affected by the relatively high NaOH and hydros concentrations. Many leuco compounds have high substantivity and level dyeing requires careful control of the dyeing temperature, the total salt concentration and gradual addition of the concentrated leuco dye vat to the dyebath. Figure 17.4 shows a typical procedure for dyeing cotton with a quinone vat dye.

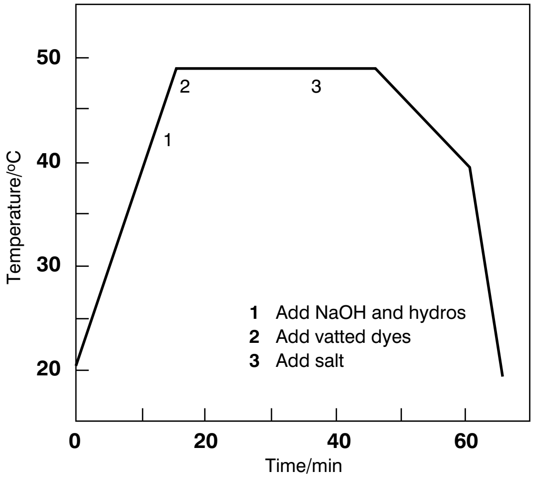


Figure 17.4 A typical procedure for dyeing cotton with a quinone vat dye

17.5.3 Problems with anthraquinone dyes

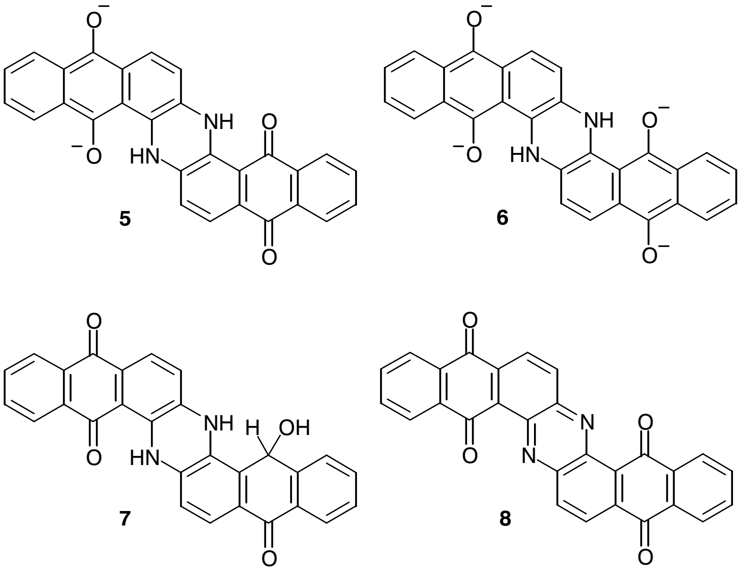
A number of chemical problems arise with some quinone vat dyes. These include:

(1) multiple reduction steps for polyquinones such as indanthrone;

(2) isomerism of leuco compounds to oxanthrones;
(3) hydrolysis of amide groups;
(4) over-oxidation after dyeing;
(5) dehalogenation of some dyes.

To minimise these types of problems, the supplier's recommendations for vatting and dyeing must be followed.

Indanthrone (CI Vat Blue 4) and some of its derivatives show a number of these problems. Indanthrone has two anthraquinone residues in its molecule. The normal blue leuco compound used in dyeing is that corresponding to the reduction of one of the anthraquinone groups (**5**, in Figure 17.5). If both anthraquinone groups are reduced, the final product (**6**) gives a brownish yellow solution, has poor substantivity for cotton and is more difficult to oxidise. Such over-reduction produces duller blue dyeings of lower colour yield. Indanthrone is also one of the quinone vat dyes whose leuco compound will tautomerise via the vat acid to an oxanthrone (**7**) if the concentration of NaOH in the solution is not sufficiently high. Oxanthrones are not easily oxidised to the parent quinone and their formation results in dyeings of poor colour yield. Mild oxidation of leuco vat dyes of the indanthrone type with hypochlorite produces a much greener azine derivative (**8**).



5 **6** **7** **8**

Figure 17.5

This is responsible for the rather poor chlorine fastness of indanthrone. The reaction is reversible and treatment of an over-oxidised dyeing with dilute alkaline hydros solution followed by air oxidation regenerates blue Indanthrone.

Partial formation of the green azine derivative can occur during air oxidation if the fabric still contains a relatively high concentration of NaOH solution. Rinsing out the excess alkali from the dyeing is therefore necessary before significant oxidation by oxygen has occurred. Some of the chlorinated indanthrone vat dyes are prone to elimination or substitution of a chlorine atom unless vatting is carried out with care. Although the indanthrone type dyes represent a rather special case, it is obvious that vatting of the insoluble pigment to produce a solution of the leuco derivative for dyeing is not always a simple operation. It is important to follow the supplier's recommendations for all stages of the dyeing process.

17.5.4 Aftertreatment of the dyeing

Once the actual dyeing process is complete, the goods go through a series of operations:

(1) rinsing to remove adhering exhausted dye liquor and chemicals. A reductive rinse with dilute alkaline hydros solution may be needed for heavy shades;
(2) oxidising the leuco dye to the pigment form using hydrogen peroxide and acetic acid;
(3) soaping at or near the boil. For soaping in a package machine, the first step may be dispersion at 60 °C to remove loose surface colour, followed by soaping at or near the boil. This is important to avoid filtration of eliminated dye particles by the package;
(4) neutralising the dyeing with acetic acid solution and final rinsing.

These processes are an essential part of the overall procedure and must be correctly carried out if the dyeing is to have the optimum fastness properties. The oxidation and soaping stages are discussed in the following section.

17.6 OXIDATION AND SOAPING AFTER DYEING

17.6.1 Oxidation

An oxidising agent has a much more positive redox potential than the compound that it can oxidise or, considered from the opposite perspective, the compound being oxidised has a more negative redox potential than the oxidising agent that it will reduce. Quinone vat dyes are generally difficult to reduce and easy to oxidise. For sulphur dyes (Section 17.11) the reverse is true. A typical vat dye has a redox potential around –0.80 V and oxidising agents with redox potentials more positive than about –0.50 V will in principle give complete oxidation of the leuco dye to the quinone. The rate of oxidation must also be acceptable. Oxidation of a leuco vat dye can be achieved by exposing the goods to air, after an initial rinse to remove adhering liquor, and therefore appears quite simple. Air oxidation, however, is of little use for compact goods such as yarn packages, and is quite slow, often requiring 30–40 min for complete oxidation. It may also result in side reactions and off-shade dyeings. Chemical oxidants are therefore generally preferred because they give more rapid and uniform oxidation throughout the material. Sodium dichromate, hydrogen peroxide, or sodium perborate or percarbonate are used at up to 40 °C. It is important that the initial oxidation is carried out under alkaline conditions to avoid forming the vat acid, which is much less soluble and hard to oxidise. Over-oxidation of some dyes, such as Indanthrone, leads to changes in hue of the dyeing (Section 17.5.3).

17.6.2 Soaping

Soaping removes pigment deposited on the fibre surface that would wash or rub off in use. The deposit is formed by oxidation of the leuco dye in the solution adhering to the fibres after dyeing. Thorough rinsing after dyeing, using a weak solution of alkaline hydros, helps to minimise this problem. Soaping involves thoroughly washing the goods in a detergent solution at or near the boiling point. It improves the light, washing and rubbing fastness of the dyeing. Some vat dyes give a slight shade change on soaping so a standardised procedure is necessary for exact colour reproducibility.

The soaping process probably involves re-crystallisation of the dispersed vat dye particles obtained from the initial oxidation of the leuco dye. This is not a spontaneous process and requires heat and water. The growth of the pigment crystals inside the cotton fibre is limited by the pore size. It is this crystallisation process that is responsible for the slight change in hue and the improvements in the fastness properties.

17.7 PRE-PIGMENTATION DYEING METHODS

In many cases, leuco vat dyes have too high a substantivity for continuous dyeing and preferential absorption by the cotton fibres would result in exaggerated tailing.

The pigment form, however, has no substantivity for cotton at all. The pre-pigmentation dyeing methods are simple processes in which a fine dispersion of the vat pigment is uniformly circulated through the goods that are then treated with alkaline hydros solution to cause reduction. Dyeing takes place around each original pigment particle with almost no migration. The dyeing is subsequently oxidised and soaped as before. Either of the two operations, the initial pigmentation or the reduction, may be batch or continuous processes. This leads to a variety of possible dyeing methods, some of which are described below.

17.7.1 Pre- and semi-pigmentation batch dyeing methods

In the pre-pigmentation method, a fine dispersion of the vat dye pigment is first circulated through the goods. In the second step, reduction to the leuco dye is carried out using NaOH and hydros. The latter may be added all at once or gradually. This method is useful for light and medium shades where levelling and penetration may be a problem in dyeing with a fully reduced vat dye. It is, however, less suitable for compact forms of material. In package dyeing, the pigment dispersion must not be filtered out in the packages but rather gradually deposited into the package by salt addition that causes the particles to slowly flocculate.

In the semi-pigmentation process, all the chemicals are circulated through the goods at room temperature before gradual heating to start reduction. The rate of vatting is very slow at the low starting temperature. As in the pre-pigmentation method, a fine dispersion is required.

The vat acid process is another alternative for package dyeing. After reduction of the vat pigment, in alkaline solution, the leuco vat acid is precipitated in the presence of a dispersing agent by acidification. This is then circulated in the goods and dyeing takes place by gradual addition of caustic soda to reform the soluble and substantive leuco form.

17.7.2 Semi-continuous processes

In semi-continuous vat dyeing processes, the fabric is pigmented by padding with the insoluble vat dye dispersion. Subsequent reduction to the leuco form is a batch operation using a jig or beam dyeing machine. Some dye comes off the fabric during development with the alkaline hydros solution and some vatted dye liquor may be added to the bath in the machine beforehand. This prevents ending in jig dyeing. In some cases, an intermediate drying of the padded fabric may be included to minimise colour bleeding into the development bath.

17.7.3 The fully continuous pad–steam process

The pad–steam process for dyeing cellulosic materials with vat dyes is a particularly important process. It involves five stages:

(1) padding the fabric with the fine vat pigment dispersion containing a wetting and an anti-migration agent;
(2) drying of the padded fabric and cooling;
(3) padding of the dried, pigmented fabric with hydros and caustic soda solution;
(4) steaming in air-free steam at about 102–105 °C;
(5) rinsing, oxidation and soaping using a series of wash boxes.

Liquid forms of vat dyes are preferred for continuous dyeing as they give less migration on drying and are more convenient for preparing the large volumes of dye liquor required. The drying of the fabric after padding ensures a high pick-up of alkaline hydros solution from the chemical pad. Some dye invariably bleeds from the fabric into the alkaline hydros solution. This is less when padding a dried fabric, and an initial addition of some dye to the chemical pad solution minimises colour tailing. Drying of the initially padded fabric is usually carried out in two steps involving a gentle pre-drying stage before the complete drying process. Pre-drying is to control migration of the pigment particles to the yarn surfaces where water is evaporating. The heating should be as uniform as possible. It is also common practice to use an anti-migrant such as sodium alginate in the first padding solution. The anti-migrant causes flocculation and aggregation of pigment particles during drying thus limiting their movement within the fabric. Some anti-migrant agents may also increase the solution viscosity. The ease of migration depends on the fibres and fabric, the solution pick-up and the pigment particle size (Section 10.5.3).

After the chemical pad, the fabric is steamed for 30–60 s in saturated, slightly superheated, air-free steam (Section 12.6.3). It is essential to avoid condensation falling onto the fabric in the steamer as this causes a spotty colour (Section 12.6.3). The steamer has a water seal at its exit with water flowing through the trough to maintain a temperature of not more than 40 °C. After steaming the fabric is rinsed by spraying to remove alkali and hydros. This is followed by rinsing, oxidation, soaping, rinsing and neutralising in a series of wash boxes.

17.7.4 Wet-on-wet processing

The usual pad–steam process cannot be used for corduroy or terry cloth because of flattening of the pile and excessive migration during drying. A wet-on-wet dyeing process is used. In this, the cloth is padded with the pigment dispersion and then, while still wet, it is padded again with the alkaline hydros solution. The solution pick-up at the chemical pad may go from values of around 70 up to 150–200%. The goods then go through the steamer and the usual aftertreatments.

17.8 FASTNESS PROPERTIES OF VAT DYES

Many quinone vat dyes provide outstanding colour fastness. The colour gamut is somewhat restricted as there are no bright colours, particularly in the red and turquoise areas. Only azoic and sulphur dyes have smaller colour gamuts. The colour gamut is the size of the 'colour space' for the colours obtainable with a particular type of dye either alone or in combinations (Section 21.8.2).

Vat dyes are very expensive, like reactive dyes. A high degree of overall colour fastness is characteristic of vat dyes. They usually have excellent fastness to washing, chlorine bleaching, alkali boiling and light. Vat dyes also have the advantage of being the only dyes for cellulosic materials that do not give shade changes on application of topical reactive finishes for cotton, such as flame resist finishes (Section 25.3.1). One minor problem is that of photochemical catalytic fading or cotton tendering by a small group of vat dyes. These are mainly yellow and orange vat dyes that photosensitise the tendering of cotton, as in drapery fabrics. The dye functions as a catalyst for the photo-oxidation of the cellulose. Others photosensitise fading of other vat dyes.

17.9 DYEING WITH INDIGO AND INDIGOID VAT DYES

Natural Indigo was rapidly displaced from the market once the synthetic product became available. The quality of natural Indigo was quite variable because of the presence of other coloured impurities. The fastness properties of Indigo dyeings are not up to the standards expected from the vat dye class as a whole. It is, however, the appearance of faded Indigo in denim that is so fashionable today. After dyeing, various wet processes, such as stone washing, deliberately enhance this faded effect. Indigo builds up primarily on the cotton fibre surface. This is one reason for the somewhat inferior fastness properties of Indigo compared to quinone vat dyes.

17.9.1 Application of Indigo to cotton

Dyeing cotton yarn for blue jeans is an important use of Indigo. In a typical batch operation, concentrated reduced Indigo is added to a dyebath from which oxygen has been removed with a little alkaline hydros. The goods are entered and fully immersed to avoid oxidation. After about 15 min at 20–25 °C, the goods are removed and well squeezed before air oxidation. Indigo does not exhaust well because of its limited substantivity for cotton, not surprising considering its small molecular size (Figure 1.4). Deep shades must be built up by repeated dipping in the dyebath after each oxidation. The use of too concentrated a dyebath is not effective for deep shades as it results in poor rubbing fastness. Some salt may be added to aid exhaustion. After dyeing, the goods are well soaped. The final dyed material may be aftertreated to produce a faded, worn look.

Continuous methods are used for dyeing ball warps, warp beams and piece goods with Indigo. This is usually carried out in a series of 4–6 wash boxes with upper and lower rollers and nips at the exits. The goods are threaded through each box and may be skyed at the mid-point. The first box is used to wet out the material. In subsequent boxes, the goods are immersed in the leuco Indigo solution for 10–30 s at a linear speed of about 25 m min^{-1}, squeezed and skyed for 2 min to oxidise the leuco dye to Indigo. The boxes are fed with a stock vat of leuco Indigo and the liquor in the boxes is circulated to maintain constant dyeing conditions. This process of several dips and oxidations is then repeated in a second series of boxes, and so on. Several rinsing and washing boxes complete the process.

17.9.2 Indigoid vat dyes

Besides Indigo itself, there are a number of other important indigo and thioindigo derivatives used for dyeing cellulosic fibres. These include chlorinated and brominated indigo and thioindigo dyes in which the nitrogen atoms of Indigo are partially or totally replaced by sulphur atoms (**9**, in Figure 17.6). Compared to the

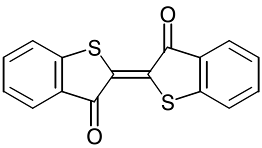


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Figure 17.6 Structure of thioindigo

anthraquinone type vat dyes, Indigoid vat dyes give much paler yellow to brown leuco compound solutions. The vatting process is also slower and requires less alkali.

17.10 SOLUBILISED VAT DYES

The solubilised vat dyes provided a means of avoiding the difficult vatting process required for quinone and indigoid vat dyes. The preparation of a solution of a leuco vat dye requires care and time, and protection of the solution from excessive exposure to air. The solubilised vat dyes avoid these problems. These dyes are pre-prepared sulphate esters of the leuco vat acid. The first product of this type was that derived from Indigo (**10**, in Figure 17.7). Later solubilised leuco dyes derived from quinone vat dyes were marketed.

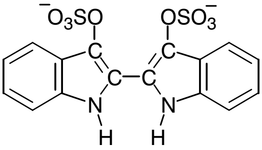

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Figure 17.7

Cotton absorbs these dyes directly from a neutral or slightly alkaline solution but they are not very substantive even in the presence of added salt. Although a leuco sulphate ester has the same negative charge as the normal leuco dye, its charge is localised in the sulphate groups whereas that of the phenolate ion is delocalised. Cotton therefore repels a leuco sulphate ester molecule more strongly than the normal leuco compound. Because of their limited substantivity, solubilised vat dyes are generally only suitable for pale shades. After dyeing, the goods are rinsed or hydroextracted to remove superficial dye solution, and the vat dye pigment is developed in the fibre by oxidation with sodium persulphate or acidified sodium nitrite solution. After neutralising with dilute soda ash solution, the goods are soaped as in the case of normal vat dyeing. The dyeing has the same fastness properties as one prepared from the original vatted pigment.

The low substantivity of the leuco sulphate esters avoids the problems of the high strike of leuco vat dyes. Since they can be used in solutions close to neutrality, they can also be used for wool dyeing. Unfortunately, the dyeing and oxidation conditions for each dye vary so it is important to follow the supplier's instructions. The use of these dyes was never widespread and has declined in recent times. They are not particularly competitive because of their high cost.

17.11 SULPHUR DYES

17.11.1 Chemical nature of sulphur dyes

Sulphur dyes are a type of vat dye used for dyeing cellulosic fibres. The insoluble pigment is converted into the substantive leuco compound by reduction with sodium sulphide and the leuco form is subsequently oxidised inside the fibre. Sulphur dyes are manufactured by heating organic materials with sodium polysulphide in aqueous or alcoholic solution, or by baking with sodium sulphide and sulphur. A variety of organic compounds are used including amines, nitro compounds, and phenols and their derivatives. These dyes almost always contain loosely bound sulphur and liberate hydrogen sulphide when treated with acidic solutions of reducing agents such as stannous chloride.

The chemistry of sulphur dyes is very complex and little is known of the molecular structures of the dyestuffs produced. The Colour Index only gives the structures of the starting materials that are used to produce these dyes and even then the information can be quite misleading. Two products manufactured from the same starting materials are unlikely to have similar properties even though they may have the same CI number. The actual dyestuffs produced from the same materials by different processes may have quite different dye contents, dyeing characteristics and environmental impacts. Because of the large amounts of sodium sulphide used in the manufacture and application of these dyes, much of which will eventually be found in the effluent, they pose a significant environmental problem. In this respect, sulphur dyestuffs produced in the developed Western nations are much more environmentally friendly.

A variety of structural units have been proposed for various sulphur dyes. It is generally accepted that these dyes are polymeric having sulphur containing aromatic heterocyclic units such as thiazines and thiazoles linked by di- or polysulphide bonds (Figure 17.8). On treatment of an aqueous dispersion of the insoluble pigment with sodium sulphide, the sulphide links are reduced forming individual heteroaromatic units with thiol groups (Scheme 17.4). These are soluble in the alkaline solution in the form of thiolate ions that have low to medium substantivity for cellulose. Over-reduction is possible if other groups are

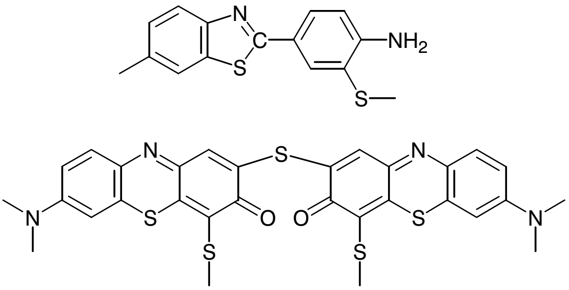

Figure 17.8 Partial chemical structures involved in dyeing with sulphur dyes

$$\text{—S—Dye—S—S—Dye—S—S—Dye—S—S—Dye—S—} + 2ne^- \rightleftharpoons n\,\bar{\text{S}}\text{—Dye—}\text{S}^-$$

Scheme 17.4

affected and the more powerful hydros is rarely used as the reducing agent. After dyeing of the cellulosic material, the thiolate ions in the fibres can be re-oxidised back to the polymeric pigment with di-sulphide bonds linking the aromatic units.

Sulphur dyes often have dull yellow vats and sulphide and polysulphide solutions are usually pale yellow. For these reasons, the colour content of a given product cannot be assessed by the usual spectrophotometric method (Section 24.1) and it is necessary to prepare dyeings and compare their colours.

17.11.2 Dyeing with sulphur dyes of various types

There are a number of different types of sulphur dye. The Colour Index lists sulphur, leuco sulphur, solubilised sulphur and condensed sulphur dyes, although the latter are no longer manufactured. The sulphurised vat dyes, which are intermediate between sulphur and quinone vat dyes, will also be mentioned in this section. Of these types, only the sulphur, leuco sulphur and the sulphurised vat dyes are of real importance in dyeing. Sulphur dyes are available as powders, pastes, and as pre-reduced liquids. The latter type is possible because a solution of a leuco sulphur dye containing sodium sulphide is much less sensitive to oxidation than a leuco solution prepared from an anthraquinone vat dye with hydros.

Leuco sulphur dyes are either solutions of the leuco dye or granular mixtures of leuco compound and reducing agent, usually sodium sulphide. They can be diluted with or dissolved in hot water and the solution used directly for dyeing, or after addition of more sodium sulphide. These dyes eliminate the difficulties of vatting, because reduction of sulphur dyes is not rapid.

Solubilised sulphur dyes are thiosulphate derivatives of the leuco compounds and are available in powder or liquid form. They are prepared by reacting disulphides with sodium sulphite to give the thiosulphate ester of the thiol. These are called Bunte salts (Scheme 17.5). These dyes are applied in the presence of alkali and reducing agent (Na_2S) to generate the sulphur dye that then undergoes further reduction to the leuco dye. Like the sulphate esters of leuco vat dyes, the thiosulphate esters have little substantivity for cotton. They are also used in paper dyeing where they are precipitated by the fillers added to the pulp.

$$\text{Dye—S—S—Dye} + Na_2SO_3 \longrightarrow \text{Dye—S—}SO_3Na + \text{Dye—SNa}$$

$$2\text{Dye—S—}SO_3Na + Na_2S \longrightarrow \text{Dye—S—S—S—Dye} + 2Na_2SO_3$$

$$\text{Dye—S—S—S—Dye} + Na_2SO_3 \longrightarrow \text{Dye—S—S—Dye} + Na_2S_2O_3$$

Scheme 17.5

The sulphurised vat dyes, such as CI Vat Blue 43 and Sulphur Red 10, bridge the vat and sulphur dye classes. They are manufactured by the same kinds of procedures as for sulphur dyes but are applied like vat dyes using hydros for vatting.

17.11.3 Characteristics of sulphur and leuco sulphur dyes on cotton

Sulphur dyes have the dullest range of colours of all dye classes but are relatively inexpensive. They are used to dye medium to deep, dull shades on cellulosic materials. There are several excellent blacks giving dyeings with good wet fastness properties. In fact, when black, and deep brown, blue and dull olive green shades are needed, with good washing and satisfactory light fastness at reasonable cost, sulphur dyes are irreplaceable. There are few green sulphur dyes and no true reds. There are, however, an abundance of blacks, blues, yellows and browns. On a world basis, sulphur dyes constitute one of the major dye classes.

Sulphur dyes are used in cotton dyeing for woven goods using jig dyeing machines and also in continuous dyeing. They are commonly used for the continuous dyeing of corduroy. They are now being used more widely in jet machines. Sulphur dyes are also used for dyeing denim olive, brown and maroon, rather than the traditional Indigo blue, as well as to 'bottom' or 'top' Indigo dyed cotton warps. To 'bottom' or 'top' means that a sulphur dye is applied either before or after the Indigo. The fastness to wet processes and to crocking can be varied almost as required to satisfy the demand for the faded look so popular for denim. This is achieved by allowing premature oxidation of the leuco dye during dyeing, by using short dyeing times so that there is inadequate time for dye penetration into the fibres, and by poor rinsing and soaping after dyeing. The dyeings can then be subsequently treated to produce the faded worn look by removing the surface colour.

Although cellulosic goods dyed with sulphur dyes usually have good washing fastness, it can be further improved by resin finishing. The light fastness varies from moderate to good in heavy shades. A major characteristic of sulphur dyes is the poor fastness to chlorine, which distinguishes them from most quinone vat dyes. Dyeings with sulphur dyes cannot be bleached with hypochlorite. In fact, these dyes are readily distinguished from other cotton dyes by their dark, dull colours and the bleaching that occurs when a dyeing is spotted with hypochlorite and allowed to dry.

Cotton dyed with some sulphur blacks becomes tendered on storing under warm humid conditions. This is a consequence of the formation of sulphuric acid from oxidation of the sulphur dye in the fibres. It can be minimised by thorough washing after dyeing before the oxidation of the leuco dye, by a final alkaline rinsing with soda ash solution, and by resin finishing. Such tendering is avoided by dichromate oxidation of the leuco dye.

17.12 BATCH DYEING PROCEDURES WITH SULPHUR DYES

17.12.1 Vatting sulphur dyes

The major reducing agent for sulphur dyes is sodium sulphide, possibly containing some polysulphides. Sulphide ion is strongly hydrolysed in solution and gives a pH almost as high as the same concentration of NaOH (Scheme 17.6). Since hydrogen sulphide is a diprotic acid, the species present in an alkaline solution depends upon the pH and may be sulphide or hydrosulphide. Polysulphide ions are all in equilibrium with themselves and sulphide and hydrosulphide ions. Formation of polysulphide ions decreases the pH of solutions of sulphide ion (Scheme 17.6). These polymeric ions are not very sensitive to air. They therefore inhibit oxidation of sulphide and hydrosulphide and help to prevent 'bronzy' dyeings with a metallic

$$S^{2-} + H_2O \longrightarrow SH^- + HO^-$$

$$S^{2-} + S \longrightarrow {}^-S{-}S^- \;+\; nS \longrightarrow {}^-S{-}S_n{-}S^-$$

Scheme 17.6

lustre and low wet rubbing fastness resulting from deposits of pigment on the fibre surfaces.

Vatting involves pasting the sulphur dye with water and sodium carbonate, diluting and adding sodium sulphide. The mixture is then boiled. Reduction is often slow. The leuco dye solution is added to the dyebath containing a small amount of hydros and caustic soda, which serve to remove any dissolved oxygen. The vatted dye is usually strained into the dyebath since sulphur dyes tend to have more insoluble impurities than other types of dye. Because of limited solubility of the leuco compounds, some dyes may have to be vatted in the bath if large quantities must be dissolved for heavy shades.

Hydros is usually unsuitable for vatting in most cases. Its use increases the risk of over-reduction, which decreases the colour yield since the over-reduced dye cannot be readily re-oxidised. Compared to vat dyes, leuco sulphur dyes are more difficult to oxidise. Alkaline solutions of glucose reduce some sulphur dyes at 90–95 °C. Reduction is achieved by the aldehyde group of the glucose. This type of reduction is much more environmentally friendly since there will be less sulphide in the dyehouse effluent. It should be used whenever possible.

17.12.2 Dyeing method

Initially the goods are wet out in the bath. Since the dyeing liquor contains appreciable amounts of sulphide, copper fittings must be avoided. If wetting or penetrating agents are used these should be of the anionic type since non-ionic surfactants form stable, non-substantive complexes with the leuco thiols. An anionic product such as phosphated 2-ethylhexanol is suitable. The bath may then be set at 40 °C with some sodium polysulphide and some EDTA. Polysulphides in the leuco dyebath prevent premature oxidation of the dye and reduce the tendency to bronziness of deep dyeings of blues, navies and blacks. An addition of a sequestrant such as EDTA avoids precipitation of the leuco thiolate by calcium and magnesium ions. The leuco dye is then added slowly and, since the leuco dyes only have low to moderate substantivity for cellulose, some salt may be added initially, or in portions during dyeing, to promote exhaustion. After dyeing the goods are rinsed, the leuco dye oxidised and the dyeing is soaped as for a conventional vat dye.

Sulphur dyes usually have acceptable substantivity, particularly in the presence of salts, so that stripping in a fresh reducing bath is not easy. Dyeing is often conducted at the boil but this decreases the degree of exhaustion. Sulphur dyes require less salt than reactive dyes and usually have reasonable exhaustion. Low sulphide leuco dyes require more salt and no polysulphide. They do not give good exhaustion in heavy shades and the use of a low liquor ratio is recommended. For popular shades such as black, it has long been common practice to use a standing bath. This is a dye bath that is re-used for subsequent dyeings after addition of more reduced dye. Any free sulphur that tends to accumulate is dissolved by addition of sodium sulphite to give thiosulphate. This prevents it sticking to the goods. The actual dyeing temperature can vary. At higher temperatures around the boil, the bath exhaustion is less but penetration of the leuco dye into the fibres is better than at lower temperatures.

17.12.3 Post-dyeing treatments

After dyeing, good rinsing before oxidation helps reduce bronziness and poor rubbing fastness by removing loosely adhering surface leuco dye solution before oxidation precipitates the insoluble pigment. Once the rinsing is completed, the leuco dye in the fibres is oxidised to the insoluble pigment.

Some leuco dyes can be oxidised in air, others need chemical oxidation. Sodium dichromate, hydrogen peroxide, or sodium percarbonate or perborate are used in warm, weakly alkaline solution. The peroxy compounds used for vat dyes can be used for sulphur dyes, but some leuco dyes (red-browns) are not oxidised by these agents. Some blues are over-oxidised, probably by oxidation of the disulphide links between the heteroaromatic units to form ionic sulphinate and sulphonate groups. This increases the water solubility, decreases the wet fastness and results in staining of other goods during washing. Even sulphur blacks oxidised with peroxides tend to be bluer, lighter and somewhat less fast to washing. The best washing fastness is obtained by oxidation of the leuco dye with sodium dichromate and acetic acid. Sodium bromate ($NaBrO_3$) is now more widely used as an oxidant, particularly in North America. It requires a small amount of metavanadate ion (VO_3^-) as catalyst for the oxidation of the more resistant red-brown dyes. This catalyst can be prepared *in situ* during sodium bromate manufacture. Commercial products usually contain this and some sodium nitrite to minimise stainless corrosion. Sodium bromate oxidation is carried out in dilute acetic acid solution at about pH 4.

Colour bronzing and crocking problems arise once a critical depth of shade has been exceeded. Deep shades must therefore be well soaped to remove residual surface colour. This improves shade stability, decreases bronziness and improves the colour brightness and washing fastness. Soaping is less critical in pale and medium depths. Unlike the quinone vat dyes, however, crystallisation of sulphur dye particles does not occur in this process. Excessively bronzy black dyeings can be treated with alkaline sodium sulphide solution to remove the surface pigment responsible for the bronzy appearance. Bronzing can be minimised by ensuring that the dye in the dyebath is always fully reduced, that the fabric is not over-exposed to air during dyeing, and that it is well rinsed immediately after dyeing. Blacks may be soaped with olive oil and soap.

Some dyeings are treated with copper sulphate, or with this and sodium dichromate, to improve the light fastness, and in some cases the wet fastness. Fabrics for use inside rubber articles should not be copper treated. Some yellow-brown dyes are treated with copper sulphate to improve light fastness but the effect is lost on washing. The use of chromium salts is now declining because of their adverse environmental impact.

Because of their dull colours, dyeings with sulphur dyes are often topped with the much brighter basic dyes. The sulphur dye pigment acts as a mordant for the cationic dyes. Dyeings with sulphur dyes may also be shaded with some sulphide stable direct dyes, but this tends to lower the washing fastness.

Alkylation of the leuco thiols under alkaline conditions with epichlorohydrin derivatives (3-chloropropene oxide) before oxidation renders them insoluble. Oxidation is then no longer required. Some dyes, however, may benefit from an oxidative treatment so as to develop the full colour. The alkylating agents may have high molecular weight or be polyfunctional so that the alkylated product has very good washing fastness in the presence of the peroxy compounds in domestic detergents.

17.12.4 Dyeing with soluble sulphur dyes

Large amounts of such dyes are sold in liquid form. They are of two types – water-soluble reduced leuco dyes, and solubilised sulphur dyes – the former being far more important. The water soluble leuco dyes are completely in solution and contain far less insoluble matter than a sulphur dye powder. This is beneficial in package dyeing. They often still require a small addition of sodium sulphide or another reducing agent. These liquids contain the stabilised leuco dye, sodium sulphoxyate-formaldehyde or sulphide and sodium carbonate. The solubilised sulphur dyes are thiosulphate esters prepared from the leuco thiols with sodium sulphite (Scheme 17.5). They usually have low substantivity for cellulose and are useful for package, padding and pad–jig applications. Reduction is necessary before or during dyeing and the usual aftertreatments are needed.

17.13 CONTINUOUS DYEING WITH SULPHUR DYES

Sulphur dyes are used for continuous dyeing of cotton goods using a pad–steam–wash process, with three groups of wash boxes for rinsing, oxidising and soaping. Padding may take place at up to 80 °C to reduce the substantivity of the leuco dye for the cotton fibres. This reduces the problems of selective absorption and the resulting initial colour tailing that it causes. As for other vat dyes, steaming is carried out in air-free saturated steam. Then the dyeing is rinsed at 40–60 °C and oxidised with sodium bromate plus metavanadate catalyst at pH 4 in the presence of acetic acid. In the remaining wash boxes, the best possible soaping and rinsing is done. For black dyes tending to produce sulphuric acid by oxidation on storage, a final soda ash rinse may be added. In some instances a better appearance results using a two-pad method. This involves padding with the sulphur dye suspension or solution, followed by intermediate drying, padding with sodium sulphide solution, steaming, and the usual aftertreatment sequence.

17.14 ENVIRONMENTAL CONCERNS

Waste sulphur dye baths, and the sulphide ion they contain, liberate hydrogen sulphide on acidification. These solutions cannot be directly released into water streams without treatment. Residual pad bath liquor from continuous dyeing is usually mixed with the residual oxidising bath liquor to oxidise the excess sulphide. Exhausted dyebaths can be oxidised with hydrogen peroxide. Oxidation of sulphide ions generates the less noxious thiosulphate and sulphate ions. This particular effluent problem can be partially solved by using glucose and caustic soda as the reducing agent but the vatting temperature must be 90–95 °C. This particular reducing system can be used with solubilised sulphur dyes, with leuco sulphur dyes as the additional reductant, and even with sulphur dyes, replacing part of the sodium sulphide.

One manufacturer has introduced new brands of low-sulphide dyes. Vatting is carried out with a new proprietary reducing agent. This acts by gradually reducing the sulphur dye as the dyeing temperature is increased so that the exhaustion is also controlled.

In addition to the present development of low-sulphide dyeing techniques using sulphur dyes, the use of chromium salts for oxidation and aftertreatment is gradually declining.

Sulphur based reducing agents such as sodium hydrosulphite and sodium sulphide are used in considerable excess to provide adequate control over the vatting and vat dyeing processes. The residues of these reducing agents and their oxidation products in the dyehouse effluent pose a serious environmental threat. Many of the difficulties associated with vat and sulphur dye reduction can be overcome by using electrolytic reduction. Since vat dyes are not soluble in water, a reduction mediator is needed. This is for example a soluble iron(III)-amine complex that is stable in alkaline solution. It is reduced at the working cathode to the Fe(II) form, whose redox potential is sufficiently negative to permit complete reduction of the vat dye pigment to its soluble leuco derivative. The reformed Fe(III) complex is then reduced back to Fe(II) at the cathode (Scheme 17.7).

$$\mathrm{Fe(X)}_n^{3+} + e^- \rightleftharpoons \mathrm{Fe(X)}_n^{2+} \quad \text{cathodic reduction}$$

$$\mathrm{QO_2}\ \text{(vat dye)} + 2\mathrm{Fe(X)}_n^{2+} \rightleftharpoons \mathrm{QO}_2^{2-}\ \text{(leuco dye)} + 2\mathrm{Fe(X)}_n^{3+}$$

Scheme 17.7

At the end of the dyeing process, the leuco compound can be re-oxidised and the insoluble vat pigment removed by filtration so that the remaining solution containing the mediator can be re-used. For sulphur dyes direct cathodic reduction is possible since a small amount of soluble leuco dye acts as the reduction mediator [2–4].

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CHAPTER 18

Cationic dyes

18.1 INTRODUCTION

Many of the initial synthetic dyes, such as Mauveine, had free basic amino groups capable of reacting with acids (Scheme 18.1). They were therefore originally named basic dyes. Molecules of these dyes are invariably organic cations and they are preferably called cationic dyes. They usually have brilliant colours and high tinctorial strength; some are even fluorescent. Many basic dyes are now obsolete because of their very poor light fastness on natural fibres but a few are still used for dyeing paper and leather and for making inks.

$$\mathrm{Dye{-}NH_2 + H^+ \longrightarrow Dye{-}NH_3^+}$$

Scheme 18.1

Cationic dyes will dye fibres with anionic sites by a process of ion exchange (Scheme 1.2). This is usually a simple direct dyeing process. Anionic auxiliary products must be avoided as they may precipitate cationic dyes in the form of an organic salt (Scheme 18.2). In dyeing protein fibres with cationic dyes, acids retard dye absorption by suppressing the dissociation of the anionic carboxylate groups in the fibres (Scheme 7.1), thus making the fibre more cationic and inhibiting adsorption of dye cations. Cationic dyes have very low substantivity for cotton unless excessive oxidation has generated anionic carboxylate groups. For dyeing cotton with cationic dyes, the cotton was usually mordanted with tannic acid fixed with tartar emetic. The insoluble, anionic tannin attracts coloured dye cations (Section 1.1.2), just as it repels dye anions when on a nylon surface after back-tanning (Section 13.9.7).

$$\mathrm{Dye^+(aq) + Aux^-(aq) \longrightarrow Dye^+{-}Aux^-(s)}$$

Scheme 18.2

Today, the major use of cationic dyes is in dyeing anionic acrylic and modacrylic fibres and, to a much lesser extent, modified nylons and polyesters. Dye adsorption by acrylic fibres involves interaction between anionic sulphonate and sulphate polymer end groups and the cationic dye molecules (Scheme 4.5). In some acrylic fibres, anionic carboxylate groups are also involved (Section 18.4.1). Disperse dyes do not build up well on acrylic fibres and are only useful for pale shades. Dyeings of natural fibres with cationic dyes invariably have poor fastness to light. In direct contrast to this, acrylic fibres dyed with cationic dyes exhibit fairly good light fastness, and good fastness to washing. The improved resistance to fading is because of the limited access of water and oxygen into the more hydrophobic acrylic fibres. Access of both water and oxygen enhance the rate of colour fading on exposure to light (Section 24.3.4). Good washing fastness of acrylic materials dyed with cationic dyes is usual since most washing procedures are at temperatures well below the glass transition temperature of the fibrous polymer and the dye is therefore less likely to diffuse out of the fibre.

18.2 CHEMICAL STRUCTURES OF CATIONIC DYES

Cationic dyes belong to a variety of different chemical classes. Many of the older basic dyes were di- and triphenylmethane, heterocyclic azine, oxazine or polymethine, or aminoazo compounds (Figure 18.1). In many cases, the cationic charge is extensively delocalised over the entire dye molecule. Typical anionic counter ions include chloride, oxalate ($C_2O_4^{2-}$) and tetrachlorozincate ($ZnCl_4^{2-}$) ions. Since the introduction of acrylic fibres in the 1940s, new cationic dyes have been developed specifically for dyeing these fibres. Many of these have quaternary ammonium groups with a localised cationic charge that is not part of the chromophore (Figure 18.1).

18.3 PREPARATION FOR DYEING ACRYLIC FIBRES

18.3.1 Preparing the material

Poor preparation of the goods is usually the major cause of poor quality dyeings and preparation should be of the highest quality consistent with the final price of the material. The preparation of acrylic fibre materials may involve desizing of woven materials, scouring and bleaching. Combined desizing and scouring are often possible since relatively soluble sizing materials such as modified starch or

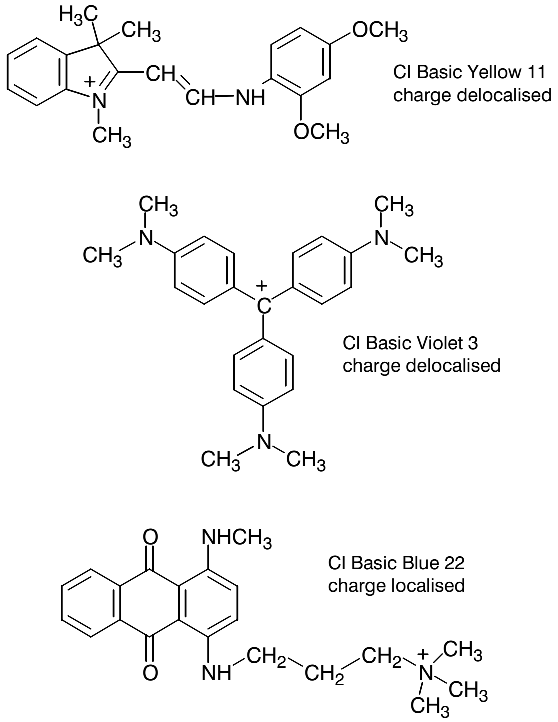

Figure 18.1 Chemical structures of some typical cationic dyes

polyvinyl alcohol are normally used. Scouring with weakly alkaline solutions of ammonia or trisodium pyrophosphate ($Na_3HP_2O_7$) is common. A non-ionic detergent is essential. Cationic auxiliary products may have substantivity for the anionic groups in the fibres and block dyeing sites whereas residues of anionic products will interact with and even precipitate the cationic dyes in the bath.

Acrylic materials sometimes have a slight yellow cast, usually a sign that drying was too severe. Bleaching is possible with sodium chlorite ($NaClO_2$) and formic acid or brightening with a fluorescent whitening agent. Some fluorescent whitening agents can be used in the presence of sodium chlorite, allowing combination of the two methods. Stabilisers that control chlorine dioxide emission (Scheme 18.3), such as borax or polyphosphates, should be used. A corrosion inhibitor such as sodium nitrate is essential when using steel equipment. Some cationic dyes are very sensitive to traces of chlorine and will rapidly fade giving poor colour yields, particularly when dyeing pale shades. An anti-chlor treatment of fabric bleached with sodium chlorite may be necessary and small additions of sodium bisulphite or thiosulphate to the dyebath will avoid problems with cationic dyes sensitive to traces of chlorine in municipal water.

$$5ClO_2^- + 2H^+ \longrightarrow 4ClO_2 + Cl^- + 2HO^-$$

Scheme 18.3

18.3.2 Dyebath preparation

The dye powder is usually pasted with acetic acid and then mixed with boiling water. Cationic dyes with delocalised cationic charges are intensely coloured and it is essential to avoid dust escaping from the powders. Concentrated liquid dyes avoid this problem. Solid forms of these dyes are often not easy to dissolve because of their tendency to form gummy material. Preparation of a paste with methanol and addition of warm or hot water is sometimes a useful alternative. Some cationic dyes are not stable in boiling water. Many react with alkali to give colourless products such as the free amine from neutralisation of an ammonium ion group (reverse of Scheme 18.1), or a carbinol by reaction of the cationic group with hydroxide ion (Scheme 18.4). Dyeing with cationic dyes therefore invariably takes place in weakly acidic solution to avoid these problems.

$$\text{Dye}^+(\text{aq}) + \text{HO}^-(\text{aq}) \longrightarrow \text{Dye—OH(s)}$$

Scheme 18.4

18.4 DYEING ACRYLIC FIBRES WITH CATIONIC DYES

18.4.1 Dyeing procedure

Acrylic fibres may contain a variety of different anionic groups. These include a limited number of terminal sulphate and sulphonate groups arising from the persulphate polymerisation initiator (Figure 3.2). In other types, there may be appreciable numbers of carboxylate groups from acrylic acid or similar comonomers added to the acrylonitrile before polymerisation (Section 4.4.1). These anionic groups are responsible for the substantivity of cationic dyes for such fibres. Figure 18.2 compares equilibrium dye adsorption as a function of pH for two types of acrylic fibres (A and B). Dyeing acrylic fibres with cationic dyes is carried

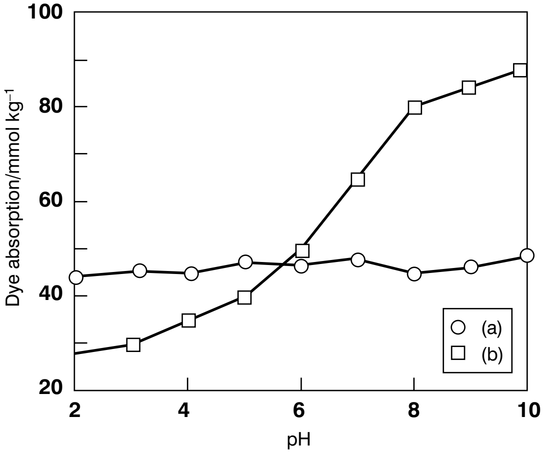

Figure 18.2 Equilibrium dye adsorption by acrylic fibres with only sulphate and sulphonate end-groups (a) and with carboxylate groups (b)

out in weakly acidic solution containing acetic acid and sodium acetate and a non-ionic wetting agent and dispersant. A small amount of sequestrant ensures that heavy metals do not interfere with chemicals in the solution.

The dye solution is often prepared by pasting with acetic acid, and a stable pH of 4.5 to 5.5 can be obtained by addition of sodium acetate to buffer the solution. Dyeing at around pH 5 suppresses the dissociation of any carboxylic acid groups in the fibre and thus controls the dyeing rate. Note the increased dye uptake of the acrylic fibre with carboxylic acid groups ((b) in Figure 18.2) as the acid groups dissociate and become anionic above pH 6. The number of carboxylate groups in an acrylic fibre varies from one type to the next. Level dyeing requires strict control of the pH and dyeing temperature, as well as the use of cationic retarding agents. The latter initially block the anionic sites in the fibre and are gradually replaced by the more substantive dye cations. An addition of up to 2.5 g l^{-1} of anhydrous sodium sulphate helps to offset the negative surface charge and sodium ions weakly block anionic sites in the fibre. Both effects decrease the initial rate of dye absorption. Sodium sulphate is not as effective as cationic retarding agents that have some substantivity for the fibre.

Figure 18.3 shows a typical dyeing procedure. If dye additions are needed to give the correct shade, the bath temperature is first slowly reduced to below 80 °C. Acrylic materials are quite thermoplastic. They easily form crack marks and creases and texturised acrylic filaments also readily lose their characteristic

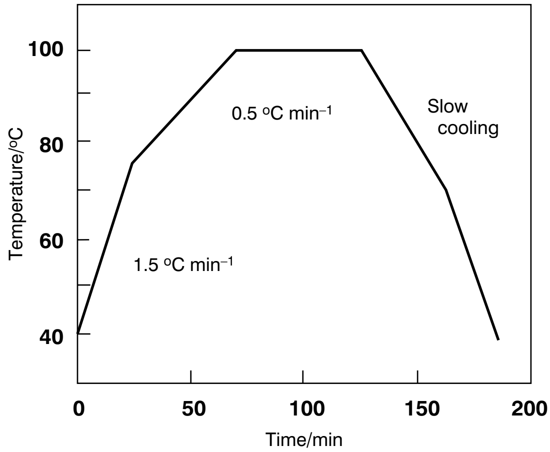

Figure 18.3 A typical procedure for dyeing acrylic material

bulk. After dyeing is complete, the bath is slowly cooled to 50–60 °C to avoid these problems. Rapid cooling by addition of cold water to the dyebath can be disastrous as it causes immediate setting of creases in the goods. The material is finally rinsed, and possibly given a mild scour with a non-ionic detergent and a little acetic acid plus a softening agent.

18.4.2 Problems in dyeing acrylic fibres with cationic dyes

Cationic dyes rapidly adsorb on all available surfaces of the acrylic fibres because of the polymer's negative surface potential in water. Once the fibre surfaces are saturated, the rate of isothermal dyeing is independent of the bath concentration and of the liquor ratio since the rate of diffusion of dye into the fibre is slow. Addition of sodium sulphate to the dyebath suppresses the rapid strike as sodium ions counteract the negative charge on the fibre surface.

Above the dyeing transition temperature (T_D) under the actual dyeing conditions, cationic dyes tend to exhaust very rapidly over a small range in temperature. Great care is needed at temperatures just above T_D to avoid unlevel dyeing. The rate of diffusion of the cationic dyes into the acrylic fibre is very slow below T_D because of the absence of the required polymer chain mobility. The rate of dyeing increases rapidly above T_D, and can double for every 2.5–3.0 °C increase in temperature. The corresponding increases in temperature needed to double the dyeing rates of nylon and polyester are typically 10 and 5 °C, respectively, but at higher temperatures for polyester. Once the acrylic fibre becomes accessible, very careful temperature control is required. For this reason, once the bath temperature reaches 70–75 °C, the rate of heating is usually significantly decreased (Figure 18.3).

The careful temperature control required when dyeing acrylic fibres with cationic dyes is necessary to avoid unlevel dyeings. These dyes on acrylic materials have at best poor migration ability. Some newer types of more hydrophilic cationic dyes have low molecular weights and lower substantivity. They migrate more readily but attempted levelling by extended heating, or heating to a higher dyeing temperature, is dangerous because of the thermoplasticity of the fibre.

If the acrylic fibre has a significant number of carboxylate groups present, the dyeing pH will greatly influence the dyeing rate. The rate of exhaustion will increase with increase in the pH as more carboxylic acid groups dissociate. Thus, it is important to know the characteristics of the particular acrylic polymer in advance.

18.4.3 Dyeing mechanism

Although a simple ion exchange mechanism explains many effects in the dyeing of acrylic fibres, the process is probably more complex than this. Over-dyeing is not usually a problem as the fibres rarely accept more dye than corresponds to the number of anionic sites. The sulphonate and sulphate groups do not change with variation of the dyebath pH but this is not true for carboxylate groups. In acidic solution, carboxylate groups are protonated and their negative charge neutralised. For dyeings carried out at constant pH, the Langmuir isotherm provides a good description of the dyeing equilibrium (Section 11.1.1). The number of anionic sites in an acrylic fibre (C_{max}) can be determined from the intercept of the graph of $1/C_f$ versus $1/C_s$ for a series of dyeings at equilibrium:

$$\frac{1}{C_f} = \frac{1}{C_{max}} + \left(\frac{1}{KC_{max}}\right) \times \frac{1}{C_s} \qquad (1)$$

18.4.4 Dyeing retarders

The presence of either cationic or anionic auxiliary products in the dyebath controls the rapid strike and high rate of dyeing of cationic dyes on acrylic fibres. Cationic retarders are organic ammonium salts with hydrophobic chains. Their adsorption on the fibre surface reduces the negative surface potential. They also compete with the cationic dye for anionic sites in the fibre, thus slowing the rate of adsorption. They have moderate substantivity for acrylic fibres and may even be adsorbed before the dye is added to the bath to decrease the strike. During dyeing, the cationic auxiliary in the fibre is gradually displaced by the cationic dye. Boiling in the presence of some cationic retarder may give some degree of levelling although this invariably increases the risk of damaging the thermoplastic material. Other types of retarder are cationic polymers that adsorb on the surface of the fibres, decrease the negative surface potential and prevent easy passage of the dye into the fibre.

Anionic retarders complex with the cationic dye in the bath (Scheme 18.2) and decrease the number of free dye molecules in solution. Such anion–cation complexes easily precipitate and an anionic agent may have a non-ionic component to keep the complex in dispersion. They are less widely used than cationic retarders. Boiling a dyeing in a blank bath containing an anionic retarder will remove some dye. For complete stripping, bleaching with hypochlorite in the presence of acetic acid at around pH 6 is possible.

18.4.5 Compatibility of cationic dyes

Dyeing on shade with mixtures of dyes is most successful when the dyes used are compatible with one another. Ideally, the colour of the dyeing builds up gradually as the dyes are adsorbed, but always with the same hue. The complex behaviour of cationic dyes in mixtures complicates the determination of their dyeing compatibility. The rate of dyeing of any given dye, under given conditions, often changes significantly when other dyes are present. The rate is also dependent on the type and amount of retarding agent present in the dyebath. The dyer must rely on the dye supplier for information on the behaviour of the dyes and must often conduct his own dyeing trials. Because many variables influence the determination of cationic dye compatibilities, different dye suppliers use different methods of evaluation.

The key parameters determining the compatibility of dyes are the fibre saturation value and the combination constant or compatibility value. Knowledge of these parameters facilitates the selection of compatible dyes. The fibre saturation value determines the amounts of cationic dye or cationic retarder that will saturate all the fibre's anionic sites. The combination constant or compatibility value is based on the rate of dyeing.

One standard test (AATCC Test Method 141 [1]) evaluates a dye's combination constant or compatibility value k, a number from 1 (rapid dyeing) to 5 (slow dyeing). Dyeings of a given cationic dye are carried out in mixtures with each dye of a standard series of five blue or five yellow dyes. The series selected will have a yellow or blue hue markedly contrasting with the test dye. Thus, a violet cationic dye would be tested in mixtures with the series of yellow dyes rather than the blue series. The five dyes in each standard series have compatibility ratings from 1 to 5. At pre-selected times during the dyeing trials with mixtures of the test and standard dyes, a piece of the dyed material is replaced by undyed material and dyeing continued. For each mixture of test dye and standard dye, the colours of the successively dyed samples are examined. The combination constant (k = 1 to 5) for the test dye is that of the standard dye for which the series of dyeings are on shade. Compatible dyes should therefore have about the same k values. This type of information is available from the dye manufacturers.

Fibre saturation values give the number of anionic sites in the fibre (mmol kg^{-1}). This value ranges from about 25 up to 115 mmol kg^{-1}. The fibre saturation value determines the % owf of cationic dye or retarder that will saturate all the anionic sites. These amounts can be calculated if the molecular weight, total cationic charge and purity of the dye or retarder are known. Consider a cationic dye powder containing 50% pure dye with a single positive charge and a molecular weight of 400 g mol^{-1}. For an acrylic fibre with 25 mmol kg^{-1} of singly charged anionic sites, 2.0% owf of dye in the dyebath will saturate all the anionic sites if the dyebath exhaustion is 100%:

$$\text{Mass of dye} = 25\frac{\text{mmol}}{\text{kg}} \times 400\frac{\text{mg}}{\text{mmol}} \times \frac{100}{50} = 20\,000\frac{\text{mg}}{\text{kg}} = 2.0\%\ \text{owf} \qquad (2)$$

Knowing how much dye will saturate the available sites in the fibre avoids excess dye adsorbed on the fibre surface, which leads to poor washing and rubbing fastness. When the total amount of dye is close to that required for fibre saturation, rapidly adsorbed dyes with low k values can block out slow dyeing dyes with high k values. For dyeing deep shades, the amount of cationic retarding agent is usually calculated so that its total charge plus that of the dye is that required to balance the charge of the fibre's anionic sites. Use of more than this quantity of retarder is wasteful and may reduce the exhaustion. The effect of cationic retarders is greater for dyes of higher k value. One of the difficulties in assessing cationic dye compatibility values is that the values are different in the presence of cationic and anionic retarders.

18.5 DYEING MODIFIED POLYESTERS AND NYLONS

Polyester modified to have anionic sites by incorporation of 5-sulphophthalic acid (Figure 4.3) has a more open polymer structure and dyes more readily with disperse dyes. Because of the anionic groups, it can also be dyed with cationic dyes. This modified polymer is also more easily hydrolysed and more sensitive to heat setting before dyeing. Heat setting is carried out at a maximum temperature of 180 °C. Dyeing is usually under pressure in weakly acidic solution at temperatures not exceeding 120 °C.

Cationic dyes diffuse quite slowly into modified polyester fibres, even with added carrier. As in dyeing with disperse dyes, the carrier serves to open up the internal molecular structure of the polymer to allow more rapid dye diffusion into the fibres. Any carrier residue must be completely removed after dyeing to avoid reduced light fastness. When dyeing two-colour effects on blends of cationic-dyeable and regular polyester, with a mixture of cationic and disperse dyes, sufficient non-ionic emulsifier must be present to prevent precipitation of the cationic dye by anionic dye dispersing and carrier emulsifying agents.

Cationic-dyeable nylon fibres are also produced by incorporation of 5-sulphophthalic acid during polymerisation. They are used mainly for tone-in-tone and multi-colour effects in batch dyeing carpets from blends of regular and modified nylons. Dyeing is carried out at the boil in weakly acidic solution. A non-ionic emulsifying agent prevents the cationic dyes from precipitating in the presence of the anionic acid dyes used for the regular nylon.

REFERENCES

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