

CHAPTER 15

Disperse dyes

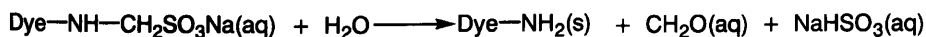
15.1 INTRODUCTION TO DISPERSE DYES

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



Scheme 15.1

contained a methylamino sulphonate group ($-\text{NHCH}_2\text{SO}_3\text{Na}$) 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).



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 ($\text{NHCH}_2\text{CH}_2\text{OH}$) 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.

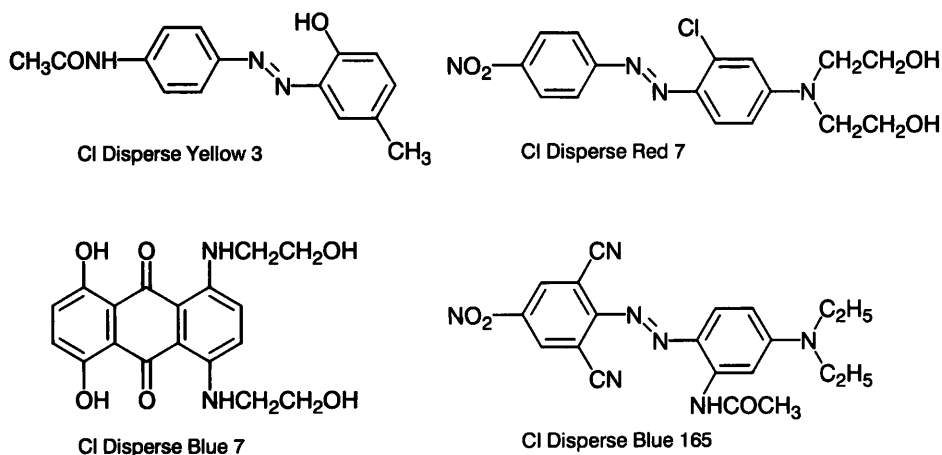


Figure 15.1 Some typical disperse dye structures

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

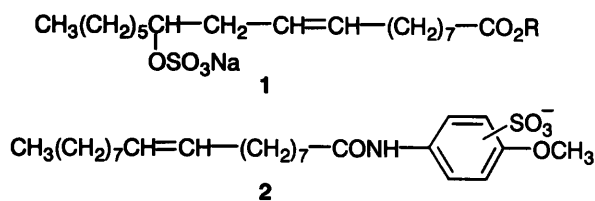


Figure 15.2 The original disperse dye dispersing agent, sulphated ricinoleic acid (1); a modern dispersant, sodium oleyl-*p*-anisidide sulphonate (2)

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

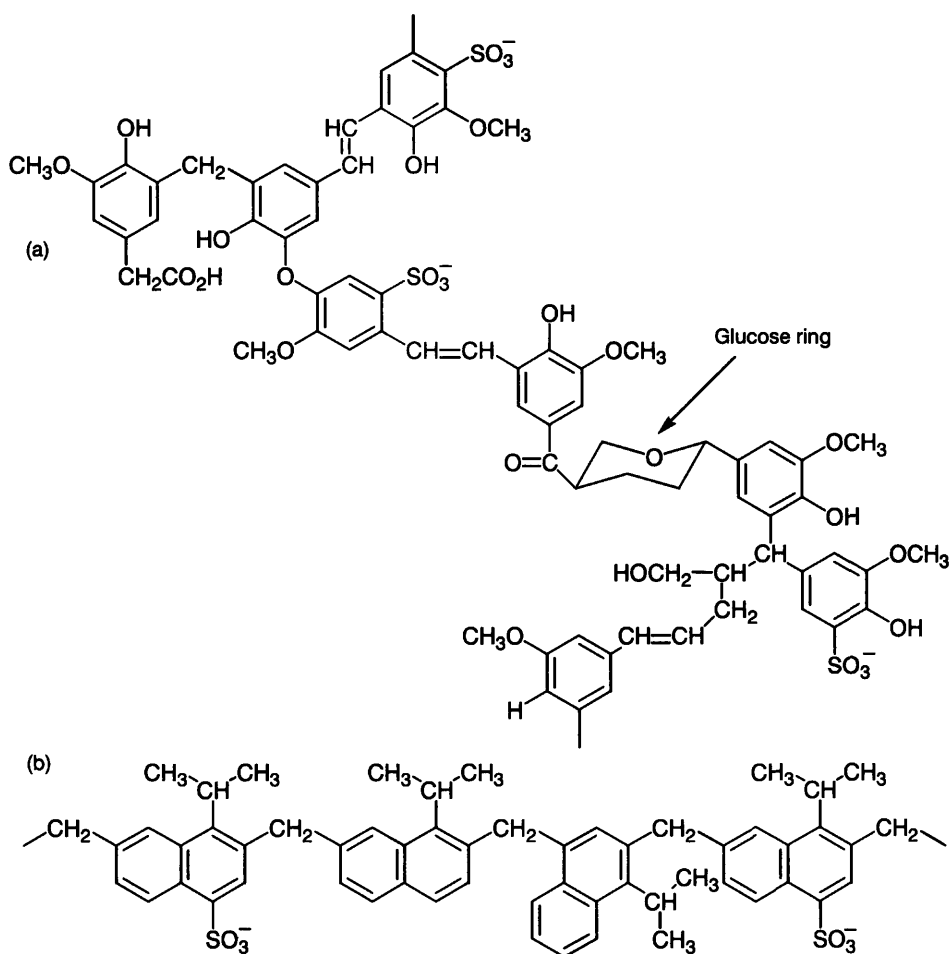


Figure 15.3 Partial chemical structures of lignosulphonate (a) and alkyl-naphthalene sulphonate-formaldehyde condensate (b) dispersing agents

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).

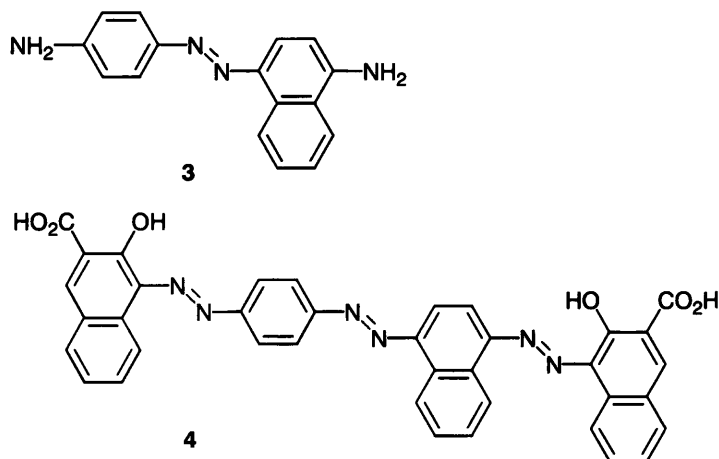


Figure 15.4 Cl Disperse Black 1 (3); dark navy pigment formed after the disperse dye is diazotised and then treated with a dispersion of BON acid (4)

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, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), 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 texturing 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.

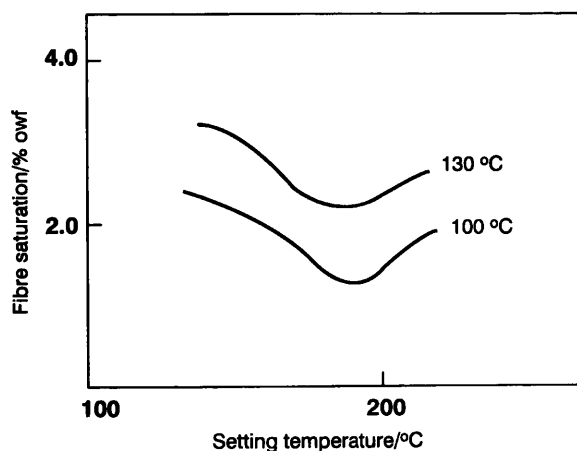


Figure 15.5 Influence of hot air setting temperature on dye uptake of polyester at dyeing temperatures of 100 and 130 °C

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.

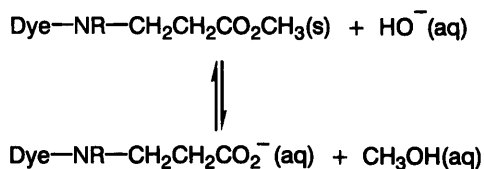
Each particular dyeing will have an optimum temperature/time profile, depending upon the type of goods, the machine being used and the dyes in the formula. A set of generalised dyeing conditions is used, however, provided that the dyebath exhaustion, the colour uniformity, and the shade reproducibility 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 ($2 \text{ g l}^{-1} \text{ NaOH}$, $2 \text{ g l}^{-1} \text{ Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) 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:

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

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 ($\text{m}^2 \text{g}^{-1}$) 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 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 $\text{Na}_2\text{S}_2\text{O}_4$ 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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