8.1.7 Dyeing of PES Fibres

PES fibres are dyed using disperse dyes, which provide a wide range of hues and display generally very good build-up and very good fastness properties on the fibres, although some dye combinations can display anomalous fastness to light and the behaviour of the dyes to heat treatments is of importance [13]. The dyes possess low, but very important, aqueous solubility that enables them to be applied to PES (and other fibres) in the form of a fine aqueous dispersion in the presence of dispersing agents. However, owing to the low diffusional rate of disperse dyes within PES fibres at temperatures upto 98 C, commercially acceptable rates of dyeing are achieved either using fibre plasticisers or *carriers* at the commercial boil (98 C) in a process referred to as *carrier dyeing* or under pressure in the region of 130–140 C in a process referred to as *high temperature* (*HT*) *dyeing*. The non-ionic, low molar mass dye molecules are volatile, a property that is utilised in their application in the vapour phase, such a process commonly being referred to as *vapour phase* or *thermosol dyeing* (see Chapter 13).

8.1.7.1 Disperse Dyes

A disperse dye is defined as *a substantially water-insoluble dye having substantivity for one or more hydrophobic fibres, for example cellulose acetate, and usually applied from fine aqueous dispersion* [123]. Whilst their main usage is in the dyeing of PES fibres, disperse dyes also enjoy usage on CA and CTA fibres as well as PA fibres (e.g. [11, 13, 124–128]). In view of the global dominance of PES fibre and its blends, which in 2012, resulted in PES fibres accounting for 55% (43.3×10^6 T) [4] of global textile demand, disperse dyes are currently the most widely used class of dye in the world, a position that seems unlikely to change in the near future. As such, it is not surprising that a very large amount of literature has been published on the chemistry, properties and application of disperse dyes.

In view of the global importance of PES fibres, this account focuses on the application of disperse dyes to this particular fibre type; the dyeing of other types of fibre using the dyes, such as CA, CTA and PA, is discussed in Chapters 7 and 9, respectively.

From the viewpoint of dyeing theory, the mechanism of the adsorption of disperse dyes, which is identical for all types of fibre (whether hydrophobic or hydrophilic), was established as a result of studies of the dyeing of CA fibres. In the following account of the thermodynamics of dyeing PES with disperse dyes, reference is also made to results obtained for the application of disperse dyes to CA and other types of fibre.

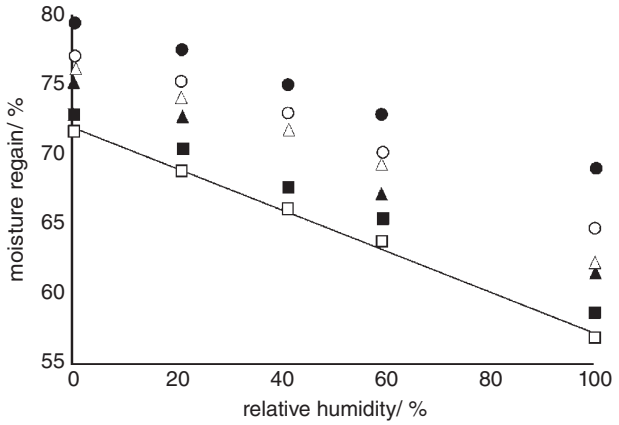
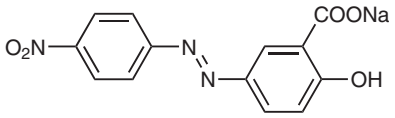


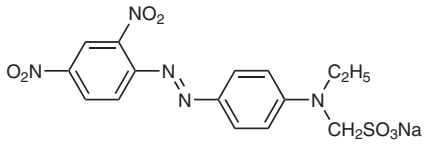
Figure 8.9 T_g of PES film as a function of RH. Symbols represent different DSC scan rates. Reproduced from [117], with permission from Elsevier.

8.1.7.1.1 Historical Aspects Disperse dyes were devised in the 1920s for the coloration of the then newly introduced hydrophobic CA fibres[5]; details of both CA and CTA fibres are given in Chapter 7. Although CA fibres are derived from cellulose and, like cotton and other cellulosic fibres such as CV, contain hydroxyl groups, they are more hydrophobic, display much lower swelling in water, possess a greater negative surface charge than cellulosic fibres and, also, are sensitive to saponification (i.e. hydrolysis of the acetyl groups) under aqueous conditions at temperatures >~85°C. Early attempts to dye the fibres revealed that both water-soluble, anionic acid dyes and direct dyes displayed little if any substantivity and, whilst basic dyes were substantive, these particular types of dye were unable to fully penetrate the fibre and the ensuing dyeings possessed low wet fastness. Attempts to enhance dye–fibre substantivity, by, for example, fibre swelling using solvents, fibre modification (e.g. saponification with alkali) and reduction in basic dye solubility via complex formation with metal salts [129] were not commercially successful.

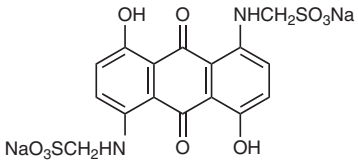


C.I. Mordant Orange 1

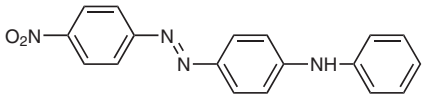
However, it was observed that some azo dyes that were devoid of sulfonate groups, such as C.I. Mordant Orange 1, were adsorbed by the substrate [130]. In addition, it was found that azoic colorants could be applied to the fibre using a procedure that was the reverse of that employed for cellulosic fibres [129, 130].[6] In this *reverse* process, the diazo component was applied prior to the coupling component; a *concurrent* application process was also devised in which the diazo component and coupling component were applied simultaneously to the CA fibre (see Chapter 7). In the reverse application of the 'ice colours' (see azoic dyes in Chapter 7), the diazo component displayed substantivity towards the fibre when applied from dispersion in the presence of a dispersing agent. Such findings resulted in the development of the *Ionamine* (British Dyestuffs Corporation, *BDC*[7]) range of temporarily solubilised disperse dyes [130, 131] as exemplified by *Ionamine Red KA* and *Ionamine Pure Blue R*, in 1922. In these dyes, which were the immediate precursors of conventional disperse dyes, water solubility was conferred by the presence of the *N*-methylsulfonate group, which, during aqueous dyeing, hydrolysed to yield the parent, low solubility azo or anthraquininoid (AQ) dye.



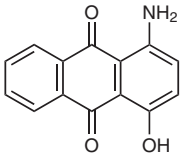
Ionamine Red KA



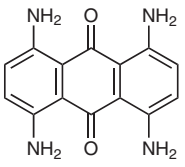
Ionamine Pure Blue R



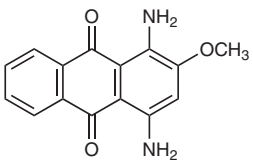
C.I. Disperse Orange 1



C.I. Disperse Red 15



C.I. Disperse Blue 1



C.I. Disperse Red 11

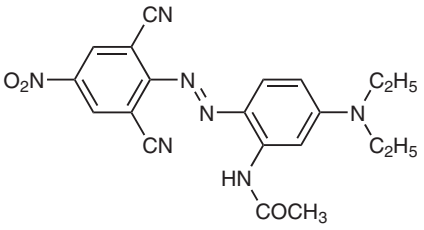
[5] often referred to as *acetate silk* fibres in early publications.
[6] this process can still be used for both CA and CTA fibres.
[7] which later became part of ICI.

Table 8.1 Solubility/mg l^{-1} of purified disperse dyes in water [155].

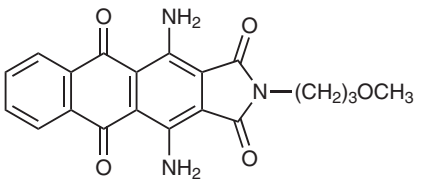
	temperature/°C			
C.I. Disperse	60	70	80	90
Red 1	1.9	3.3	5.6	10.6
Red 15	2.6	4.1	5.4	12.8
Yellow 1	16.4	35.2	75.2	154
Orange 5	3.3	5.3	9.8	23.3

Members of this dye range could also be diazotised *in situ* and developed (e.g. with a phenol or an amine) to provide another shade. This dye range was superseded by the *SRA*[8] (British Celanese Ltd) [132–136] and *Duranol* (BDC) ranges of disperse dyes that were applied to the CA fibres in the form of fine aqueous dispersion, as exemplified by *SRA Orange 1* (C.I. Disperse Orange 1), *SRA Red VII* (C.I. Disperse Red 15) [137], *Duranol Blue CB* (C.I. Disperse Blue 1) and *Duranol Red X3B* (C.I. Disperse Red 11) [138, 139]. Several methods were devised to disperse these early disperse dyes which resulted in the dispersing method that is currently employed for modern disperse dyes [13]. The subsequent introduction of the more hydrophobic CTA and PES fibres resulted in considerable developments in disperse dyes [140–147].

8.1.7.1.2 General Characteristics of Disperse Dyes The chemistry of disperse dyes has been widely discussed (e.g. see [140–143, 145, 146, 148–154]); the dyes belong to several chemical classes of dye, predominantly azo (e.g. C.I. Disperse Blue 165) and AQ (e.g. C.I. Disperse Blue 60) types.



C.I. Disperse Blue 165



C.I. Disperse Blue 60

8.1.7.1.3 Aqueous Solubility The most important features of disperse dyes in relation to their application from an aqueous medium are their low solubility in water and the fact that the dyes are applied from fine aqueous dispersion.

The aqueous solubility of disperse dyes has been discussed in Chapter 3. Briefly, whilst disperse dyes do not contain ionic groups, the typically low molar mass compounds possess polar groups (e.g. —NH_2, —OH and C_2H_5OH) which impart a small, but vitally important aqueous solubility to the dye molecules. Although dye solubility is small at low temperatures, it increases with increasing temperature [155–158] (Table 8.1).

Merian *et al.* [159] demonstrated that the aqueous solubility of disperse dyes increased with increasing temperature over the range 80–130°C, in some cases by a factor of ~30. Broadhurst [11] reported that the aqueous solubility of disperse dyes at 130°C can be expected to be ~3.5 times greater than that at 95°C. Typical values for the solubility of pure disperse dyes are quoted as ranging between 2 and 100 mg l^{-1} [160] and ~8 and >400 g l^{-1} at 130°C [161]. The aqueous solubility of disperse dyes varies depending on the physical form of the colorant, as well as the method of determination, being lower for pure, crystalline dye compared to finely divided, commercial dye forms [161]. The solubility of disperse dyes has a major effect on both the rate of dyeing and dye migration, empirical equations having been devised that relate solubility to these two particular dyeing characteristics [159].

The effects of dispersing agents on the solubility of disperse dyes from the viewpoint of dye adsorption are discussed in Section 8.1.7.1.10.4.

[8] *SRA* was derived from the particular dispersing agent used to disperse the dyes namely *sulphoricinoleic acid*.

8.1.7.1.4 Dye Classification Although the SDC proposed a series of tests to express the dyeing behaviour of disperse dyes on CA [162], CTA [163] and PES [164] fibres, no universal classification system is employed for disperse dyes and dye makers tend to characterise their products on the basis of, for example, sublimation characteristics or energy level, as well as end-use requirements, as exemplified by dyes intended for use on automotive fabrics for which very high light fastness is required, or work-wear, for which high wet fastness is demanded, high-visibility clothing, etc., as well as printing.

8.1.7.1.5 General Dye Properties in Relation to Dyeing Many disperse dyes are sensitive to pH, which can result in hydrolytic degradation during aqueous dyeing; the hydrolysed form of the dye may display different substantivity and be of different shade to the parent non-hydrolysed variant. Whilst such pH-induced changes are sometimes reversible, alkaline conditions cause permanent dye deterioration (e.g. [13]). Inconsistencies in the shade of some disperse dyes can arise owing to the presence of some metals (Cu and Fe) for which a sequestrant can be employed; the effect of metals on shade varies for different dyes [13]. Some types of dispersing agent promote reduction of azo disperse dyes during the HT dyeing of PES. To minimise the reductive degradation of the dyes, the aqueous dyeing of PES fibres is normally carried out from a slightly acidic dyebath (pH ~4.5–6.0); reduction inhibitors may also be used. However, selected disperse dyes are suitable for application at high pH (pH ~9.5), for example in the dyeing of PES/cellulosic fibre blends with disperse and reactive dyes, for which specific buffers are commonly employed [165].

When PES fibres dyed with disperse dyes are subjected to heat treatment (e.g. heat setting and pressing), the dye molecules may migrate within the substrate and accumulate at the fibre surface. Such *thermal migration* (aka *thermomigration*), which can impair the wet fastness properties of the dyed material, is influenced by various factors including the structure, formulation and concentration of the dye, fibre linear density, thermal conditions used (temperature, duration and type of heating) as well as the presence of finishes [166].