

## Dyeing with Disperse Dyes

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### 1. Introduction

Before the First World War, almost all dyes were applied from solution in an aqueous dyebath to substrates such as cotton, wool, silk and other natural fibres. However, the introduction of a man-made fibre, cellulose acetate, with its inherent hydrophobic nature, created a situation where very few of the available dyes had affinity for the new fibre. Water-soluble anionic dyes had little substantivity for the fibre and the alkaline conditions required for the application of vat dyes brought about a loss in tensile strength and deterioration in fibre appearance due to the rapid hydrolysis of acetyl groups.

The development of disperse dyes for dyeing secondary cellulose acetate fibres in the early 1920s was a major technological breakthrough although their major use today is for the coloration of polyesters, the most important group of synthetic fibres (Broadbent, 2001). The first systematic study of dyes that was suitable for application to cellulose acetate by a direct dyeing process was carried out by Green. The presence of hydroxyl and amino groups, a low relative molecular mass and an almost neutral or basic character were found to be advantageous. As a result of these investigations, in 1922, Green and Saunders developed the Ionamine Dyes (British Dystuffs Corporation) for application to acetate fibres (Green & Saunders, 1923; Green, 1924) (Fig. 1). These water-soluble dyes were hydrolyzed in the aqueous dyebath to produce the sparingly soluble free base in a very fine suspension that was then absorbed by the fibre. This discovery, that aqueous dispersions of almost water-insoluble dyes were highly suitable for the dyeing of secondary acetate, led to the rapid development of other such dyes for dyeing cellulose acetate.

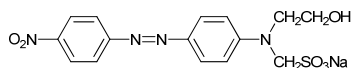


Fig. 1. An Ionamine dye.

In 1923, aqueous dispersions of dyes were examined independently by the British Celanese Corporation and the British Dyestuffs Corporation and Ionamine dyes were superseded by ranges of disperse dyes, such as SRA (British Celanese Corporation) and Duranol (ICI), that were devoid of ionic solubilising groups (Fig. 2). These sparingly water-soluble acetate dyes were applied to cellulose acetate in the form a fine aqueous dispersion (Burkinshaw, 1995). The advent of other man-made fibres, such as nylon in 1938 and acrylic in the early 1940s, both of which possess a significant hydrophobic nature, further increased the use of disperse dyes. However, it was the discovery in 1941 and subsequent commercial introduction in

1948, of polyester fibres that triggered an intensive research effort into disperse dyestuffs. Due to the highly crystalline and hydrophobic nature of polyester, the fibre is only slightly swollen by water up to the atmospheric boil which, in the 1950s was the maximum practical temperature available for dyeing. Consequently, new methods of application had to be developed. These new methods involved opening up the fibre structure temporarily so as to facilitate dye penetration (Fourness, 1979).

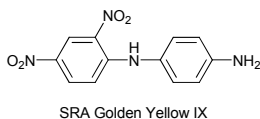


Fig. 2. SRA range dyes by British Celanese Corporation.

When cellulose acetate is dyed at 85-95°C, small molecular size dyes are required which have an adequate solubility to dissolve and diffuse into the fibre. Such dyes possess high vapour pressure that did not normally cause a problem as the resulting dyeings were not usually subjected to high temperatures. However, with the advent of polyester fibres, problems with fastness arose due to dye sublimation during the subsequent heat setting and pleating processes. The vapour pressure of disperse dyes is related to the relative molecular mass of the dye and can therefore be decreased by increasing the relative molecular mass of the dye and by incorporating polar substituent groups into the dye molecule, such as benzoyl or amide groups. Incorporation of polar groups into the dye molecule causes a slight increase in water solubility in addition to increasing the relative molecular mass, thus giving rise to slower rates of diffusion. The decrease in rate of diffusion means that dyeing times have to be increased. However, the use of higher temperatures or carriers leads to increases in the rate of diffusion of dye molecules into the fibres.

## 2. Disperse dyes

Disperse dyes are traditionally non-ionic chemicals with sparing solubility in water which, consequently, are able to retain comparatively better substantivity for hydrophobic fibres, such as polyester, nylon and acetate. For the sake of efficient diffusion into textiles, the particles of disperse dye should be as fine as possible comprising low molecular weight molecules in the range of 400 – 600. It is essential for disperse dyes to be able to withstand various dyeing conditions, pH and temperature, resulting in negligible changes in shade and fastness (Aspland, 1992, 1993).

Disperse dyes are often substituted azo, anthraquinone or diphenylamine compounds which are non-ionic and contain no water solubilising groups. The dye particles are thus held in dispersion by the surface-active agent and the dyes themselves are called disperse dyes. They are marketed in the form of either an easily dispersible powder or a concentrated aqueous dispersion and are now the main class of dye for certain synthetic fibres (Ingamells, 1993).

### 2.1 Classification

In the 1970s, ICI developed a method for the classification of disperse dyes according to their sublimation fastness and dyeing properties, placing them into categories named A to D. Class A dyes had low relative molecular masses and hence poor sublimation fastness, but

desirable dyeing properties, whereas Class D dyes had high relative molecular masses and therefore good sublimation fastness, but somewhat poorer dyeing properties. Classes B and C were between these two extremes. Other dye manufacturing companies such as BASF soon introduced their own similar systems of disperse dye classification.

The Disperse Dye Committee of the Society of Dyers and Colourists has now classified the dyeing characteristics of disperse dyes according to the results of several tests which can be performed on the dyes. These tests assess characteristics such as the build up, levelling properties, rate of dyeing and temperature range properties of the dyes on a range of hydrophobic fibres. 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 (Broadbent, 2001).

A chemical classification by chromogen is very useful to dye chemists, particularly those who intend to synthesize dyestuffs, while the latter classification is more valuable for dyers. The Colour Index listed around 1,150 disperse dyes in 1992 by chemical class. i.e. azo, anthraquinone, meethine, nitrodiphenylamine, xanthene, aminoketone, quinoline and miscellaneous.

### 2.1.1 Azo disperse dyes

Azo dyes are defined as compounds containing at least one azo group attached to  $sp^2$ -hybridized carbon atoms, such as benzene, naphthalene, thiazole and thiophene. Under normal conditions, azo dyes exist in the more stable planar *trans*-form so that the carbon-nitrogen bond angle is approximately  $120^\circ$  (Fig. 3) (Gordon & Gregory, 1983).

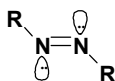


Fig. 3. The *trans*-form of an azo dye.

Azo dyes are by far the most important class and account for more than 50% of the total commercialized disperse dyes in the world. There are several reasons why azo dyes have dominated the markets and have replaced many of the conventional anthraquinone dyes. In principal, the azo group is an inherently intense chromophore in terms of the tinctorial strength, when compared with the comparatively weak anthraquinone chromogen, normally 2 or 3 times stronger in tinctorial strength. By virtue of their simplicity and the ease of manufacture, unlike the other types of dyestuffs such as anthraquinone and styryl, the cost of manufacturing azo dyes is comparatively lower than the expensive anthraquinone dyes.

Azo dyes cover a whole gamut of colours, from yellow to blue-green hues, by varying the intermediates especially when heterocyclic diazo components are coupled to aminobenzene couplers substituted with powerful electron donating groups, giving bright blue-green colours. Although some deficiencies of azo dyes are not easily overcome, such as duller shades, lower fastness to light and breakdown into carcinogenic amines derived from the cleavage of the azo linkage, and have somewhat restricted their extensive usage against anthraquinone dyes, the cost effectiveness undoubtedly compensates for the drawbacks mentioned above (Gordon & Gregory, 1983).

Aminoazobenzene dyes, which can be represented by the general structure (Fig. 4), have been by far most important disperse dyes particularly during the early period of progress for the coloration of polyester fibres.

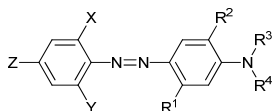


Fig. 4. General structure of aminoazobenzene dyes.

As a typical donor-acceptor chromogen, the electron-accepting substituents, X, Y and Z and the electron donating substituents R<sup>1</sup> and R<sup>2</sup> are favourably sited to create visible colors from yellows to reds, and more recently, blues (Fig. 5). In general, aminobenzenes are easily diazotized by normal diazotization reagents and the resultant diazonium salts are comparatively stable so that high yields of dyes of good purity are obtained.

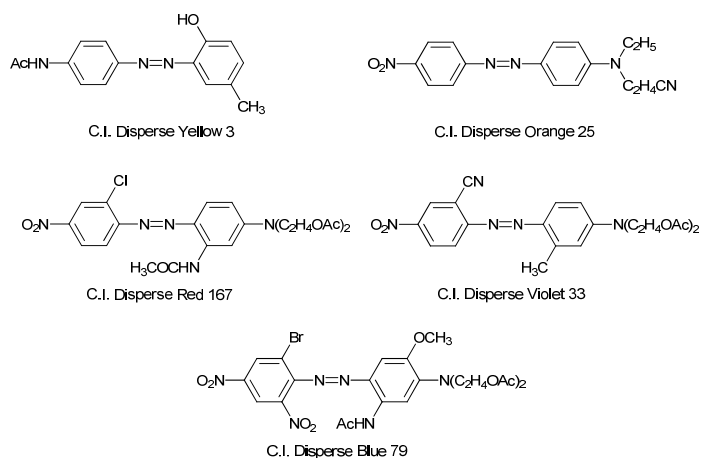


Fig. 5. Some typical azo disperse dye structures.

### 2.1.2 Anthraquinone disperse dyes

Anthraquinone disperse dyes were among the early 'acetate' dyes and have made an important contribution to the violet and blue shade range. They produce bright dyeings of excellent light fastness and cause no dye stability problems during dyeing.

From a historical point of view, anthraquinone dyes are the oldest to mimic a natural chromogen. As seen from the Colour Index Classification, anthraquinone systems of basic formula (Fig. 6) are second only to the azo chromogen for the manufacture of disperse dyes.

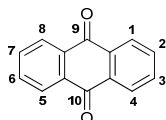


Fig. 6. Anthraquinone systems of basic formula ; 9,10-anthraquinone.

A whole range of colour shades from yellow to even turquoise blue can be provided by variation of the substituents in different positions. Thus, 1,5-dihydroxyanthraquinone has a yellow shade and an absorption maximum at 425 nm, whereas 1,4,5,8-tetraaminoanthraquinone absorbs maximally at 609 nm, giving rise to a greenish-blue color. The inherent brightness of anthraquinone dyes, which exceeds that of typical azo dyes, may be accounted for by their unique fluorescence emitted by the transition from the first singlet excited state to the ground state (Gordon & Gregory, 1983).

Simple anthraquinone disperse dyes containing alkylamino or hydroxy groups (e.g. C.I. Disperse Violet 4, C.I. Disperse Red 15) can be used for the coloration of cellulose acetate, although of limited color range and of moderate fastness. When more hydrophobic substituents are introduced to enhance the affinity for polyester fibre, various shades can be produced. Among these types of anthraquinone dyes, a bright red dye (C.I. Disperse Red 60) and a violet dye (C.I. Disperse Violet 26) have been widely used in the coloration industry, particularly C.I. Disperse Red 60 which acts as a basic colour for trichromic combinations in pale shades and is one of the best dyes available for heat transfer printing. These dyes show exceptional brilliance and high light fastness against similar colours of azo dyes (Fig. 7).

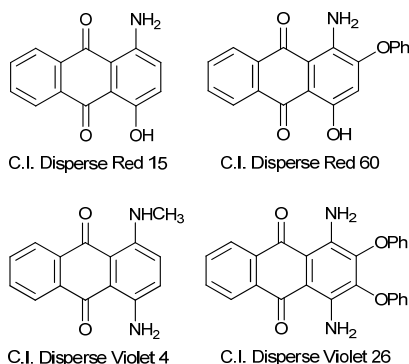


Fig. 7. Commercial anthraquinone disperse dyes.

Recent literature has revealed that more bathochromic shifts can be obtained by condensing various arylamines with 4-arylamino-5-nitro-1,8-dihydroxy anthraquinone or with 4,8-dichloroquinizarin or 4,5-dinitrochryszazin to give deep blush-green shades on polyester (Peters & Chao; Yu & Chao]. Although anthraquinone disperse dyes have many advantages such as bright shades, high light fastness, good stability in dyeing and excellent levelling, serious economic drawbacks and inevitable pollution problems ensure the continuing displacement of these dye by other types, such as benzodifuranone dyes and azo dyes having heterocyclic diazo components (Griffiths, 1984; Weaver & Shuttleworth, 1982).

### 2.1.3 Other disperse dye classes

Although anthraquinone, monoazo and disazo disperse dyes are the most important classes of disperse dyes in terms of market share, there are a number of other important classes as follows ;

- Nitroarylamino disperse dyes
- Coumarin disperse dyes

- Methine disperse dyes
- Naphthostyryl disperse dyes
- Quinophthalone disperse dyes
- Formazan disperse dyes
- Benzodifuranone disperse dyes

## 2.2 Constitution and fastness properties

Many attempts have been made to trace relationships between the chemical structure of a dye and its fastness properties. However, such inter-relationships can be very complex. Some general trends can be distinguished but, within these, more subtle interactions involving electronic and steric effects make it very difficult to set down hard and fast rules. In recent years, more precise information has been obtained by studying groups of very closely related dyes in which minor structural changes have been shown to influence fastness properties.

Satisfactory fastness to light, washing, rubbing, sublimation and (on acetate) burnt gas fumes, is particularly significant for disperse dyes (Dawson, 1984).

### 2.2.1 Fastness to wet treatment

The demand for environmentally friendly dyes of high wet fastness on polyester is increasing. As a result of current trends towards the increased use of finishing treatments, microfibers and stringent wash fastness test criteria, previously satisfactory colorants are no longer suitable and the performance of agents of relatively high fastness can be rendered ordinary (Choi et al).

Fastness to washing is similarly dependent on diffusion as it is unlikely during the limited time of a washing cycle or test that an equilibrium between the dye inside and outside the fibre will be reached. Consequently, the fastness will be subject to kinetic control: other things being equal, increases in size and polarity of the dye molecule will reduce its mobility within the fibre and be reflected in a lower diffusion coefficient and an attendant increase in wash fastness. The nature of the disperse-dyed substrate is also very important. Polyester tends to have better fastness to wet treatments such as washing and perspiration fastness than nylon and acetate with a given dye since its structure is more crystalline and hydrophobic. Both properties restrict diffusion, the former directly, by presenting a close-packed structure as an obstacle to movement, and the later directly by reduced fibre-swelling which serves to keep the structure tightly packed. Heat fastness/dyeing trade-off, changes in diffusion characteristics to improve wash fastness will have an opposite effect on dyeability.

In terms of providing satisfactory wash fastness on polyester, dye selection has become far more critical than it ever has been, because of the more demanding wash fastness tests employed currently and the now widespread use of aftertreatments. Before the 1970s, the universal wash-fastness trial for dyed polyester was the ISO 105 C03 wash test, which simulated domestic washing with soap and examined staining on polyester and cotton or wool. Nearly all disperse dyes gave very good to excellent results. However, from the 1970s onwards, achieving satisfactory fastness to washing became more problematic as the result of a customer-driven rise in standards being implemented in the guise of more severe testing protocols (Baldwinson, 1989). Stringent conditions were stipulated in the late 1960s by Marks and Spencer, who required their suppliers to use only those dyes that met criteria using adjacent nylon, which showed a greater tendency to stain than wool or cotton. Heat

treatments made fastness more of a problem in the case of some dyes; the high temperatures lead to thermomigration where dye molecules tend to move from the core of the fibre towards the surface, and thus counteract the reduction clearing and lower the wash fastness. In the early 1980s, an official range of European wash test (the ISO 105 C06 series) was published that reflected the widespread adoption of detergents for domestic laundering, which with dyed polyester often gave lower ratings than with soap-based tests: any dye stripped from the fibre by the soap tends to remain solubilised through the powerful surfactant properties of the soap present in a relatively large concentration. Detergent, containing much less surfactant, is able to remove surface dye, but is not as effective at solubilising it, promoting staining although the inclusion of perborate bleaching agents can counteract this. This together with the now routine use of multifibre adjacent fabrics, has rendered many previously satisfactory dyes unsuitable and made dye selection far more important in this respect. An extreme requirement is that for polyester microfibres: the high surface area to mass ratio of these materials means that higher than normal depths of dyeing are needed for satisfactory shades. An investigation has suggested that planar dyes of low relative molecular mass (for satisfactory build up) and of high tinctorial strength may meet the challenge (Chao & Chen, 1994). During the 1990s, the development of novel wash test procedures has continued in order to counter perceived changes in the market such as innovations in detergent formulation. The appearance of a new generation of protocols like BS 1006 UK-TO and ISO 105:C08 is a sign that fastness criteria will keep evolving and so present fresh challenges to which disperse dye technology must respond (Choi et al, 2000).

A range of test has been devised to simulate the action of various other wet agencies including perspiration. Much effort has been expended on trying to find ways to mimic human sweat, which is a complex mixture containing salt and amino acids (Heir et al, 1946). Fresh perspiration is slightly acidic, but goes alkaline with bacterial action (Perspiration Fastness Subcommittee, 1952), hence the development of two test, one at pH 5.5, the other at pH 8. Disperse-dyed polyester generally performs well because its structure is still close-packed at body temperature (the level at which the test samples are maintained).

Recently, improved wet fastness was achieved by incorporating easily washable groups into dye structures. Thus, the modified dyes containing diesters, thiophenes, benzodifuranones, phthalimides and fluorosulfonyl group have been designed to improve the wash fastness (Fig. 8) (Koh & Kim, 1998a, 1998b; Koh & Greaves, 2001). The most often patented dyes with enhanced wash fastness and build-up properties were based on heterocyclic amines such as 2-aminothiophene, and 2-aminopyrazole, and were used separately or in combination (Freeman and Sokolowska, 1999).

### 2.2.2 Fastness to dry heat

Sublimation, or dry heat, fastness can be an important property of disperse-dyed polyester because of the use of heat treatments in the finishing of the fabric; disperse dyes must be small, non-ionic molecules of low molecular weight. As such, they often exhibit a significant vapour pressure. Therefore, if heat treatments during fixation, or subsequently, e.g. ironing, are involved, the dye may sublime and cause contamination of equipment or adjacent undyed material (Gordon & Gregory).

The heat fastness of dyeings of equal dye concentration on the same substrate will, at a specific temperature and time, be dependent on the size and polarity of the molecules of the

dyes involved which in turn determine the rate of diffusion of the dye within the substrate and the volatility of the dye. Increases in size and/or polarity will tend to reduce the rate of diffusion out of the fibre and the vapour pressure of the dye and thus increase sublimation fastness. The same changes will tend to make application by exhaustion methods more problematical as the lowered diffusion coefficient will mean slower fibre-penetration, reduced levelling power and lower colour yields. Therefore, a compromise between the decrease in hydrophobicity (and consequent loss in fibre affinity) and polarity has to be made. Because of this property, disperse dyes have been classified into types of excellent dyeing properties but poor heat fastness (Class A) through to those with excellent heat fastness but poor dyeing properties (Class D) (Nunn, 1978).

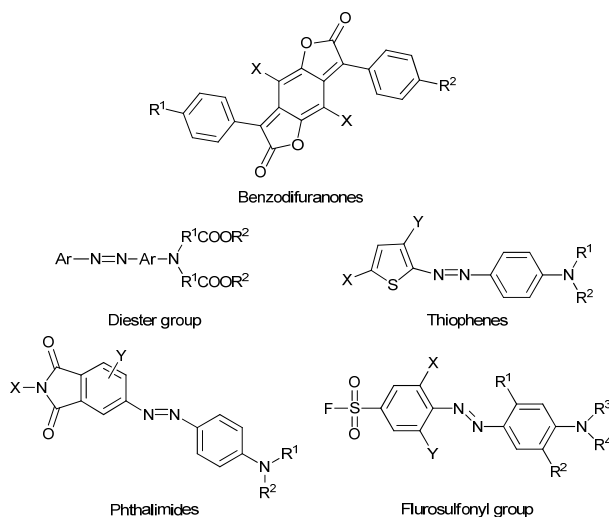


Fig. 8. Recently developed disperse dyes with high wash fastness

The structural changes useful in raising heat fastness include modification of the side chains of the terminal amino nitrogen (Hallas, 1979). However, other balances must be kept in mind; the hydroxyl group is a particularly effective group, but can have an adverse effect on light fastness on polyester. Increasing mass may also play a small part in the effectiveness of these groups. A 2-acetyl amino group in the donor ring can have a beneficial effect on heat fastness (Gordon & Gregory, 1983), the tendency to sublime decreasing as the polarity and the number of potential hydrogen-bonding groups increases.

Generally the effects of substitution in the diazo residue are less marked. Replacement of either carbocyclic ring for a heterocycle can raise fastness, as well as substitution on the heterocycle itself, although in some cases, little difference has been found, for example between some thiazole and phenyl analogues (Peters & Cheung, 1985).

Improved sublimation fastness can be achieved by increasing the molecular size and by incorporating additional hydrophobic groups into anthraquinone ring. Thus, the modified dyes such as C.I. Disperse Red 92 and C.I. Disperse Red 229 have been designed to improve the moderate sublimation fastness of C.I. Disperse Red 60 by introducing additional substituents that leave the brilliant hue intact (Fig. 9).



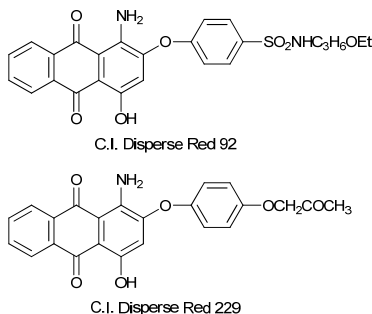


Fig. 9. Modified dyes for improved sublimation fastness.

### 2.2.3 Fastness to light

Many dyes are known to fade when left exposed to sunlight for prolonged periods. Such photofading is a well known technological phenomenon within the textile industry (Zollinger, 1991). In particular, certain applications of textiles dyes require higher light fastness quality control than others and this has led to an accepted light fastness scale that facilitates selection of a dye for a give application (Oakes, 2001). Although a close relationship does exist between the chemical structure of a dye and its light fastness rating, it is important to remember that other factors are of relevance, the most critical of which are (Giles & McKay, 1963):

- a. The inherent photostability of the dye molecule; in general, the chromophoric nucleus is the most important element in determining the light fastness of a dye, but nuclear substituents may alter the fastness significantly.
- b. The concentration of the dye within the fibre; usually the fastness of a dyed fibre increases with increasing dye concentrations.
- c. The nature of the fibre in which the dye is dispersed; different fibres contain different chemical groups and these substituents can have a significant effect on the light fastness rating of a dye on a given fibre.
- d. The wavelength distribution of the incident radiation; not all the absorption are equally effective in starting a fading process.
- e. The composition of the atmosphere; the moisture content of the atmosphere can have a marked effect on the fading rates of certain dyes.

A survey of commercial disperse dyes applied to various substrates has revealed that the average light fastness is highest on polyester, followed by di-, tri-acetate and then nylon, although this could simply be an artefact of commercial usage and research concentrating on dyes for polyester and acetate as these are the more important substrates for this dye class.

However, anomalously low fastness arises with *o*-nitro substitution. The deleterious effect has been ascribed to the proximity of the negative charge on the nearest oxygen of the nitro function to the azo group preventing electron delocalization, ultimately lowering the bond order of the  $\alpha$ -nitrogen-carbon link and therefore increasing susceptibility to photolytic cleavage (Mehta & Peters, 1981).

In the 4-aminoazobenzene series, variation of the terminal amino groups provides an important means of increasing light fastness on polyester. The use of  $\beta$ -cyanoethyl groups appear advantageous, while that of  $\beta$ -hydroxyethyl groups, useful in dyes for diacetate, is

here inexpedient, although *o*-acylation brings about a striking increase in fastness (Kassim & Peters, 1973)

Oxidation and reduction reactions are known as the two most important pathways for the fading of dyes. Although photooxidative processes are generally accepted as being responsible for fading on non-protein substrates, such as polyester and acetate, there is little direct evidence (Fig. 10).

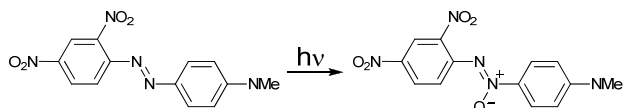


Fig. 10. Oxidative fading mechanism of azo dye : the conversion of the azo group to an azoxy group.

Deductions from Hammett plots provide indirect affirmation (Gordon & Gregory, 1983) as well as increased fading in the presence of oxygen. Direct evidence has however been obtained of an oxidative pathway, the dealkylation of 4-*N,N*-dialkylaminoazobenzenes on polyester and nylon in which dye-sensitized singlet oxygen attacks the terminal nitrogen lone pair electrons of the dye in the ground state. While the dealkylated products will not differ radically in colour, the creation of carbonyl species and peroxides may cause destruction of the azo group, leading to more significant fading.

Intensive investigations have concentrated on improving the molecular stability to light, and elucidating some empirical correlations between the electronic behaviour of substituents and their resistance to light. Anthraquinone dyes containing electron-donating substituents are more susceptible to fading than those containing groups, such as  $\text{-NHCOPh}$ , which contribute towards better light fastness (Dawson, 1983).

Further incorporation of less basic substituents, notably heterocyclic moieties, into  $\beta$ -positions of 1,4-diaminoanthraquinone leads to bright turquoise blue dyes, for example C.I. Disperse Blue 60 and Blue 87 that were originally developed by DuPont and BASF in 1955 and 1963, respectively (Fig. 11). The superior light fastness of these dyes is attributed to the electron-withdrawing effect exerted by the imide groups (Dawson, 1983). These two bright dyes are still preferred for the coloration of polyester in intrinsic turquoise shades and in a bright green by the addition of an appropriate yellow dye.

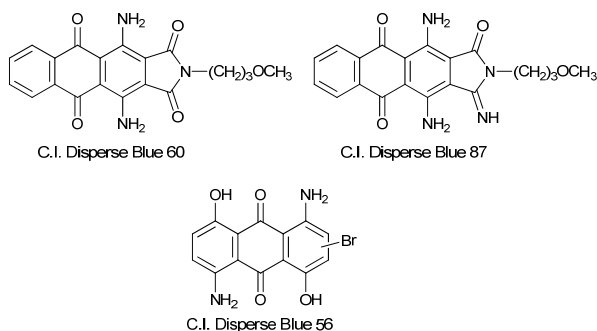


Fig. 11. Modified dyes for improved light fastness.

A classic anthraquinone dye, C.I. Disperse Blue 56 was first synthesized to dye cellulose acetate during the late 1950s, featuring a bright neutral blue shade and excellent level dyeing. However, the manufacture of this dye gives rise to environmental problems and is economically disadvantageous. Nevertheless, this dye remains of limited application in areas that require good light fastness in pale depths.

### 3. Hydrophobic fibres

Disperse dyes can be applied to a whole range of chemically diverse, hydrophobic man-made fibres, which include acetate, acrylic, modacrylic, nylon, polyester and polyurethane fibres. However, of these, the most important fibres for disperse dyeing are polyester and secondary cellulose acetate (J. R. Aspland, 1997).

#### 3.1 Polyester fibres

Polyester fibre is a manufactured fibre composed of synthetic linear macromolecules having in the chain at least 85% (by mass) of an ester of a diol and benzene-1,4-dicarboxylic acid (terephthalic acid) (Denton & Daniels, 2002). Fibres of the most common polyester, Poly(ethylene terephthalate) (PET or PES) is generally made from either terephthalic acid or dimethyl terephthalate together with ethylene glycol (Fig. 12) (Lewin & Pearce, 1985).

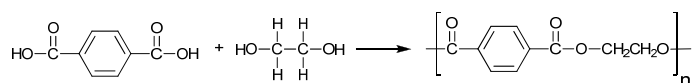


Fig. 12. Polymerization of poly(ethylene terephthalate).

##### 3.1.1 Historical background

The first commercial fibre-forming polyester was developed by Dickson and Whinfield working at the Calico Printers' Association in England in 1941. It was produced by condensation of ethylene glycol and terephthalic acid. Rights to manufacture this product were bought by ICI and DuPont. The ICI product was named Terylene and the DuPont product Dacron (A. D. Broadbent).

Polyester fibres are produced as medium- and high-tenacity filament yarns and as staple fibres of various lengths and fibre colour to suit the kinds of spinning machinery found in the textile trade. Polyester fibre not only offers the typical features of a synthetic fibre, such as high chemical resistance, high moth-proofness, excellent wash and wear and permanent press characteristics, but also, when blended with cotton and wool, gives rise to fabrics of high quality. These unique properties make it the largest commodity fibre in the synthetic fibre world, in 1990, polyester production exceeded the total production of both polyamide and polyacrylic fibres (Brunnschweiler & Hearle, 1993).

Recent developments include new polymer compositions, physical characteristics improvement, enhanced aesthetic quality and improved dyeability (Fig. 13). Developments in physical characteristics include decreasing the fibre's intensity so as to facilitate the rupture and removal of objectionable 'fuzz balls' (pilling-resistant fibre) and anti-static finishing through the application of the hydrophilic finish which creates capillarity in the interfibre spaces (Brunnschweiler & Hearle, 1993). As for improvements in dyeing properties, modified polyester has been introduced that contains ionic sites to facilitate ionic

dye attachment as well as the use of a copolymer that lowers the compact structure of polyester (Moncriff, 1970). To increase the aesthetic quality of textured yarns, high refractive index inorganic particles have been incorporated into fibres and silk-like polyester fibre have been developed (Brunnschweiler & Hearle, 1993). However, although these modifications enhanced the lustre of polyester, softness in handle was lacking. During the 1970's and 1980's, the 'touch' of polyester fibre was enhanced; alkali deweighting treatments were used to make the fibre more delicate and a wrinkle finish imparted it to an appearance similar to that of silk. In addition, there have been many other activities in fibre development, such as polymer modification, fibre blending, surface treatment, the mixture of various fibre cross sections, special spinneret design and fine denier spinning for polyester and silk-like fibre developments (Brunnschweiler & Hearle, 1993).

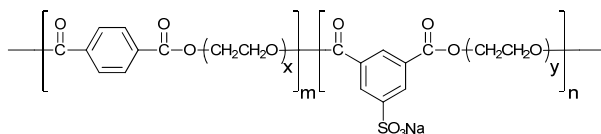


Fig. 13. Modified polyester dyeable with cationic dyes.

### 3.1.2 Properties of polyester fibres

#### Physical properties

Polyester fibres are very hydrophobic, therefore, they absorb only a very small amount of water and there is no significant change in their tensile properties when they are wetted. The moisture regain of polyester fibre is approximately 0.4% at 65% relative humidity and 20°C (Moncriff, 1970). Polyester materials dry quickly because of their very low water absorption.

The tensile properties of polyester fibres vary with temperature; at 180°C, the fibre retains approximately half the tenacity it possesses at room temperature and its extensibility increases (Nunn, 1979). Medium-tenacity yarns shrink by approximately 6% in boiling water but only by 3% in hot air at the same temperature; similar differences are found at higher temperatures. Polyester fibres will, however, take a permanent-set when distorted at high temperature (Moncriff, 1970)

Polyester fibres exhibit high initial moduli of elasticity, high resistance to blending deformations and good recovery from them, negligible creep under the low extensions to which the fibres are most commonly subjected in use and high resistance to abrasion [65].

Polyester can be exposed to sun light for 600 hours and the fibre strength will still be around 60-70% of its original strength (Moncriff, 1970).

#### Chemical properties

Polyester fibres show outstanding resistance to damage by most common chemicals under ordinary conditions of exposure and a wide range of substances have little or no effect on their strength.

Their resistance to oxidizing and reducing agents is excellent and, as a consequence, bleaching treatments using sodium chlorite, sodium hypochlorite or hydrogen peroxide may be employed. Concentrated formic acid, acetic and oxalic acids produce strength losses

of 15%, 6% and 8%, respectively, after treatment at 80°C for 72 hours, but dilute solutions of mineral acids are resisted, even at 100°C.

Polyester fibres can be treated with dilute alkalis at temperatures up to 100°C and can withstand the strongly alkaline conditions used in vat-dyeing and or in mercerizing. However, solutions of caustic alkalis do, in fact, attack and hydrolyze the polymer, but at temperatures up to the boil, such attack is confined to the surface of the fibre; this particular characteristic has been utilized in the production of silk-like polyester.

Polyester polymers display the typical reactions of ester and can be hydrolyzed in the presence of dilute alkali or acid or by water alone. No serious change can be expected to be observable in the textile-processing properties of fibres and yarns dyed for one to two hours at 130°C, so long as the pH of the bath has been maintained close to 7. However, in an acidic bath of pH substantially less than 4 or in an alkaline bath, more rapid attack will occur. Above pH 8, high-temperature dye baths can induce serious degradation of polyester fibres if treatment is prolonged (Nunn, 1979).

### 3.2 Acetate fibres

Cellulose acetates are esters of cellulose in which a large fraction or even all the hydroxyl groups have been esterified using acetic anhydride. The two major types of cellulose acetate have about 55 and 62% of combined acetic acid. These values correspond to cellulose with degree of substitution of 2.48 and 3.00, respectively. The latter is called cellulose triacetate, and the former is called cellulose diacetate (Fig. 14) (Broadbent, 2001).

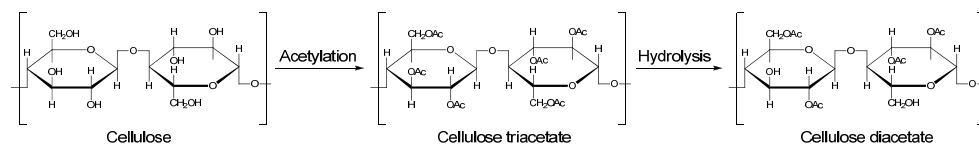


Fig. 14. Chemical structures of acetate fibres

Acetate fibres belong to the class of man-made cellulosic fibres and are manufactured by treating cellulose in the form of pure wood pulp or, less frequently, cotton linters, with a mixture of glacial acetic acid and acetic anhydride at low temperature in the presence of an activation catalyst such as sulphuric acid, perchloric acid, zinc chloride or similar salts (Rouette, 2000). Cooling prevents an increase in temperature of the mixture that will promote excessive hydrolysis of the cellulose. This initial product is cellulose triacetate (primary cellulose acetate) and cellulose diacetate (secondary cellulose acetate) is obtained directly from the triacetate by partial hydrolysis (Broadbent, 2001).

Cellulose diacetate, once widely known by its producer's company name, Celanese, can be written and drawn in a similar manner to cellulose, except that between 77-80% of the hydroxyl groups have been acetylated by reaction with acetic acid, to give cellulose acetate esters (Trotman, 1984).

#### 3.2.1 Historical background

Acetate was the first hydrophobic man-made fibre, and when it appeared on the market, knowledge about the mechanism of dyeing and of molecular structure of fibres was limited. Because acetylation makes the fibre hydrophobic, resistant to swelling, and endows it with a

greater electronegative surface charge in water, there is no response to direct dyes. The absence of basic groups affords no sites of attachment for acid dyes, but the yarn does show some substantivity for basic dyes. In the early days, limited ranges of water-soluble dyes, selected from a variety of sources by trial and error, were placed on the market. In many cases both their fastness and exhaustion left much to be desired (Trotman, 1984)

Cellulose di- or triacetates have no ionic groups. They are quite hydrophobic fibres. When introduced in the 1920s, cellulose diacetate was initially difficult to dye satisfactorily with existing ionic dyes. Fine dispersion of simple, non-ionic azo and anthraquinone compounds, of limited water solubility, however, efficiently dyed this fibre. These so-called disperse dyes are slightly soluble in water and are extracted from the aqueous solution by the solid fibre in which the dyes are quite soluble (Broadbent, 2001).

### **3.2.2 Properties of acetate fibres**

#### **Physical properties**

These fibres in no way resemble fibres of cellulose. Both cellulose diacetate and triacetate are relatively hydrophobic and thermoplastic. The standard regains of cellulose di- and triacetate are 5.0 and 2.5%, respectively. They hardly swell in water (Broadbent, 2001).

Cellulose diacetate is thermoplastic in the hot dyebath and care should be taken to ensure the goods are not subjected to stretching. They are approximately 40% weaker wet than dry, and their extensibility is increased by about 40% when wet. They are permanently glazed at temperatures above approximately 175°C, soften at 205°C and melt at approximately 230°C. The low temperature of softening may be of advantage for embossed finishing (Trotman, 1984).

The mechanical properties of triacetate fibres are close to those of the secondary acetate but they do not lose a great deal of strength when wet. It gives fabrics with a firm crisp handle, less soft than that of the diacetate (Broadbent, 2001)..

#### **Chemical properties**

Both cellulose acetates are resistant to dilute solutions of acids but are sensitive to alkaline solution, which cause hydrolysis of the acetate ester to hydroxyl groups, especially at higher temperatures. The triacetate is more hydrophobic and more compact and crystalline than the diacetate and has better resistance to alkaline solutions and to solvents (Broadbent, 2001).

## **4. Disperse dyeing**

For dyeing polyester fibres, in practical terms only disperse dyes are suitable. Through their hydrophobic properties, these dyes are capable of penetrating into the similarly hydrophobic polyester fibre. This class of dyes has only extremely poor solubility in water (Rouette, 2000); for this reason, dispersing agent is added to the dyebath to maintain dispersion stability, especially in the case of high temperature dyeings (Burkinshaw, 1995).

### **4.1 Basic principle**

The inclusion of dispersing agent in the dyebath is a crucial factor in the application of disperse dyes. Once such a compound is added to water, its dual character results in the formation of micells above critical, but low, concentration. The hydrophobic tails of the

dispersing agent molecules are inside the micelle which, as a consequence, is able to solubilise the disperse dye molecules, so conferring a higher apparent solubility on the dye. The dye transfer to the fibre from the micelles. As micelles empty their dye, they re-form and dissolve more dye from the solid particles (Ingamells, 1993)

Much of the evidence that is available on the subject suggests that in dyed polyester fibres the disperse dyes are present chiefly in the monomolecular state [Schroeder & Boyd, 1957; Hoffman et al, 1968]. At the end of the dyeing process, the dye that has been absorbed by the fibre is in a state of dynamic equilibrium with the dye that remains in the bath, and the fraction of the latter that is in aqueous solution must be present in the same state of aggregation as the dye in the fibre. It is reasonable to infer that the transfer of the dye to the fibre takes place from a monomolecular aqueous solution, the concentration of which is maintained during the first phase of the dyeing process by the progressive dissolution of solid dye from the particles in dispersion in the bath. In the presence of dispersing agents the following equilibrium situation is set up (Fig. 15) (Johnson, 1989).

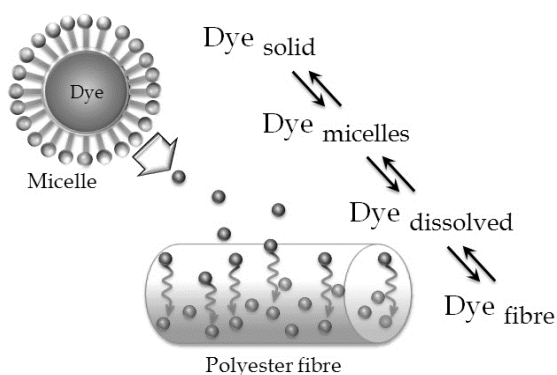


Fig. 15. Disperse dyeing mechanism

The four stages of the process mechanism are as follows (Murray & Mortimer, 1971):

- Some of the dyes dissolve in the water of the dyebath.
- Molecules of dye are transferred from solution to the surface of the fibre.
- The solution in the dyebath is replenished by the dissolution of more solid material from the dispersion.
- The adsorbed dye diffuses monomolecularly into the fibre.

The process of transfer from the aqueous solution to the fibre is comparable with the extraction of a solute from one solvent by a second, immiscible solvent and similar laws of partition are applicable. Distribution coefficients that are related to the solubilities of the dyes in the aqueous and fibre phases can be determined for different processing temperatures, although they may be affected by the simultaneous equilibrium between the aqueous and solid phases of the dye. The rates of the first and second stages of the process mechanism are governed by these solubilities.

It was established that the disperse dyeing system was truly reversible and that the results conformed to a rectilinear isotherm. Typical results show linear relationship in distribution of dye between polyester and water. It is well established that dyeing with disperse dyes is

the transfer of dye molecules from a molecular dispersion into the fibre and because of the linearity of the isotherms obtained, the amount of dye adsorbed  $[D]_{ad}$  relative to the concentration in the bath  $[D]_s$  can be expressed by a partition coefficient  $K$  (A. Johnson, 1989), i.e.

$$\frac{[D]_{ad}}{[D]_s} = K \quad (1)$$

As more dye is introduced into the system a point will be reached at which the amount of dye in the dyebath at equilibrium exceeds the solubility of dye. In the ideal case further additions of dye will produce no further change in the concentration of dye in solution, and hence no change in the concentration of dye on the fibre. At this point, therefore, if the abscissa denotes total dye in the bath rather than dye in solution, then the isotherm will become horizontal (A. Johnson, 1989).

Dye molecules that have been adsorbed on the fibre surface diffuse into the interior of the fibre by a relatively simple mechanism, which appears to obey Fick's equation (Patterson & Sheldon, 1959). That is to say, the rate of diffusion of dye through unit area (transverse to the direction of diffusion) at any point in the fibre is directly proportional to the concentration gradient of the dye at that point. As would be expected, the amount of dye taken up by polyester fibres from a bath of constant concentration is found to be proportional to the square root of the dyeing time, until a saturation value is approached. Very similar results are observed during the earlier stages of the process in dyebaths of normal composition and concentrations, such as are employed in commercial 'exhaust-dyeing' processes. It is found that the rate of dyeing is quite independent of the concentration of the dyebath, practically up to the point at which equilibrium is established (Waters, 1950). For dyeings carried out at a constant temperature, a plot of the instantaneous fractional 'dye uptake' ( $C_t/C_\infty$ ) against time of dyeing gives a steeply-rising asymptotic curve, which appears to fit a law based on the hyperbola or, possibly, on the hyperbolic tangent (Cigarra & Puente, 1967).

An important difference between the dyeing behaviour of polyester fibres and that of other fibres such as nylon and secondary acetate, which also accept disperse dyes, is in their rates of dyeing. Polyester fibres dye very slowly at temperatures much below 100°C (Waters, 1950). Disperse dyes can be applied to cellulose secondary acetate readily over approximately 1 hour at 80°C. Higher temperatures are avoided as otherwise acetate groups on the cellulosic fibre can be hydrolysed to hydroxyl groups, which can spoil the surface of the fibres and reduce their substantivity towards the disperse dyes. Cellulose triacetate is more difficult to penetrate with disperse dyes because of its more compact molecular structure, but it can be dyed at the boil. Nylon fibres can be dyed under conditions similar to those used for cellulose acetate fibres. In case of acrylic fibres, the presence of anionic groups such as  $-\text{SO}_3\text{H}$  and  $-\text{COOH}$  permit only pale shades to be obtained under normal conditions with disperse dyes (Ingamells, 1993).

#### 4.2 The effects of variations in disperse dyeing

Several factors affect the dyeing of polyester fibre with disperse dye such as crystal form of the dye, dispersing agents, particle size of the dye, pH of the dyebath, temperature of dyeing and heat setting, and fibre fineness.



### **Crystal form of the disperse dyes**

The possible different crystal forms (e.g.  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  and  $\epsilon$ ) of disperse dyes have been suggested to influence the saturation values achieved on polyester, due to differences in the vapour pressure and solubility of the different forms of dye in both water and fibre (Biedermann, 1971, 1972).

### **Dispersing agent**

Disperse dyes are sparingly soluble in water and often crystalline with varying particle size. These characteristics are inadequate for dispersing the dyes in water and cause unlevel dyeing. In order to achieve the required particle size and distribution (Heimanns, 1981), the disperse dye is milled, usually in the presence of a dispersing agent (Derbyshire et al, 1972). Generally, the dispersing agents are anionic, ligninsulphonates or polycondensates of arylsulphonic acids with formaldehyde which facilitate milling by preventing agglomeration of the dye particles.

### **Particle size in dispersion of the dyes**

The aqueous solubility of disperse dye particles in a dispersion increases with decreasing particle size (Kenneth & Skelly, 1973). Thus an increase in the severity of milling that accompanies a reduction in the particle size of the dye enhances the solubility and adsorption of disperse dye.

### **pH of dyebath**

Generally, in the commercial dyeing of polyester fibres with disperse dyes, dyeing is carried out within the pH range 5.5 to 6.5. Strongly alkaline or acidic conditions, such as higher than pH 9 and lower than pH 4, induce hydrolysis of the fibre as well as decomposition of azo disperse dyes (Nunn, 1979). In the case of high temperature dyeing, this degradation of polyester fibre and dye is accelerated.

### **Substantivity of disperse dyes**

The substantivity of disperse dyes towards polyester fibres is one of the most critical factors in determining dyeing behaviour and there have been many studies carried out to evaluate the substantivity of disperse dyes towards hydrophobic fibres, including polyester, in order to select suitable dyes. These attempts include the 'Solubility Parameter Concept' (Ingamells, 1990) and 'IOR (Inorganic/Organic) values' (Kim et al, 2003).

### **Temperature**

The adsorption and diffusion of disperse dyes on polyester are greatly influenced by temperature as an increase in temperature increases the mobility of the polymer chains in the amorphous regions of the fibre. Polyester fibres dye very slowly at temperatures much below 100°C. At 85°C, the temperature normally used for the dyeing of secondary cellulose acetate, it was found that polyester fibre dyed at rates between 700 and 1000 times slower than those measured for the same dyes on secondary cellulose acetate and nylon (Nunn, 1979). When, however, sufficient time was allowed for the polyester fibre to come nearly to equilibrium with the dyebath, it was found that it had taken up approximately the same amount of dye as had secondary acetate and in most cases about twice as much as nylon (Waters, 1950). For the dye-hydrophobic fibre system, the affinity of the disperse dye decreases with increase in dyeing temperature while the saturation value of the dye in the fibre increases with increasing temperature (Bird et al, 1959; White, 1960).

Heat setting changes the morphology of the polyester fibres. When fabrics of polyester are heat set in air under conditions of free shrinkage, the dye exhaustion first decreases and then increase with increasing setting temperature. The minimum exhaustion occurs after seeing at around 160-190°C. 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 (A. D. Broadbent, 2001).

### Fibre fineness

Much attention has been given recently to dyeing microfibres. In a broad sense, especially in Europe, the term microfiber means fine fibers of less than 1.0 denier. However, in South Korea and Japan, where fine-fibre technology is more advanced, fine fibres of 0.04 – 0.4 denier class are generally used in this filament area (Koh et al, 2006). A useful preliminary relationship between the percentages of dye on weight of goods ( $C_1$ ,  $C_2$ ) needed to achieve a particular depth of shade on polyester fibres of two different fineness ( $D_1$ ,  $D_2$ ) was suggested by Fothergill (Fothergill, 1944):

$$\frac{C_2}{C_1} = \sqrt{\frac{D_1}{D_2}} \quad (2)$$

According to this equation, it takes much more dye to dye the microfiber to the same apparent depth as the regular fibre. Therefore, such marked denier difference can affect dyers in a number of ways (Aspland, 1997).

### 4.3 Recent requirements in disperse dyeing technology

Environmental issues have been gaining importance in all aspects of industrial production (McCarthy, 1998), and various legislative requirements have emerged with increasing regularity to reduce the impact of dyeing processes on the environment. In response, the industry has been forced to become increasingly innovative in order to develop new products and practices that are more environmentally friendly than existing ones (Lewis, 1999). Therefore, innovation and developments in color chemistry and dyeing will allow the colorist to meet ever-increasing environmental restrictions, produce novel effects, and reduce processing costs (Leadbetter & Leaver, 1989).

The demand for environmentally friendly dyes with high wet fastness on polyester is increasing, and the so-called alkali-clearable disperse dyes suggest a promising new direction (Fig. 8). These alkali-clearable disperse dyes obviate the need for sodium hydrosulphite and significantly reduce the cost of effluent treatment (Koh & Greaves, 2001). Recently, these types of dye have become technically important for the coloration of polyester and its cellulosic blends. They perform well on international standard and commercial wash fastness test (such as ISO C06 C2S) (Choi, 1999).

To achieve acceptable levels of wet fastness after post-heat treatment, the development of modern disperse dyes must be directed towards satisfying a number of needs. Firstly, new dyes need to be tailored towards satisfying shorter, more easily reproducible and more economical dyeing processes. Secondly, with the increasing use of polyester and polyester blends in sports and leisurewear, there is a clear demand for dyes of higher wet fastness. Indeed this requirement has become even more important with the introduction of polyester microfibres, where higher depths of shade have to be dyed in order to obtain the same visual yield as with conventional polyester fibre. Finally, the development of new disperse

dyes must take into account the effect that effluent from the dyeing process will have on the environment, and aim to minimize such pollution. These objectives are not mutually exclusive but interrelated; they must all be taken into account in any dye development program (Leadbetter & Leaver, 1989).

## 5. Main methods of disperse dyeing

Disperse dyes are the most important class of dye used in dyeing polyester fibres and provide a wide range of hues with good build-up and fastness properties adequate for most purposes. The rate of dyeing may be raised to the level of commercial acceptability, either by raising the working temperature to the region of 130°C, or by dyeing at the boil in the presence of an accelerating agent or 'carrier' (Waters, 1950). Disperse dyes can also be transferred to polyester fibres under dry conditions by impregnating the goods with a suitable dispersion, drying and then baking at temperatures in the range 190-220°C (Ingamells, 1993).

### 5.1 Carrier dyeing

The term 'carrier' is originated from the idea that the compound and the dye formed a complex which could 'carry' the dye into the fibre, thus causing more rapid dyeing. It is now known that the carrier is adsorbed by the fibre and operates by modifying the structure of the amorphous regions (A. Johnson, 1989).

A carrier is an organic compound, dissolved or emulsified in the dyebath. Carriers allow dyeing of even deep shades at the boil within a reasonable dyeing time. Common polyester dyeing carriers include butyl benzoate, methyl-naphthalene, dichlorobenzene, diphenyl and *o*-phenylphenol, the latter two being the most popular.

The actual mechanism by which a carrier accelerates dyeing has been widely debated and probably depends on 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, thus promoting polymer chain movements and creating free volume. This speeds up the diffusion of the dye into the fibre.

A typical carrier dyeing procedure involves running the goods in the bath 60°C and adding dilute dispersing agent, emulsified carrier and lastly the disperse dyes. The temperature is then gradually raised to the boil and dyeing continued at this temperature (A. D. Broadbent, 2001). The sorped carriers must be removed from the polyester after dyeing, usually by hot-air drying the goods from 150-180°C. Residual carriers can adversely affect lightfastness if left on the goods.

The benefits of carriers were overwhelming in the early days of polyester dyeing because polyester fabrics could be dyed in unpressurized becks with no more dyeing problems than with direct dyes. However, carrier dyeing has steadily declined since the development of suitable machines for dyeing polyester under pressure at temperature around 130°C. Carriers are still used in some garment and small commission dyehouses where high temperature pressurized dyeing machines are not available (A. D. Broadbent, 2001).

### 5.2 High temperature dyeing

High temperature dyeing is the most widespread method of batch coloration. The temperatures (ca. 130°C) require pressurized equipment and impart increased diffusion of

the dyestuff (and therefore increased rate of dyeing) by reducing cohesion between polymer chains and increasing the kinetic energy of the dye molecules. A typical exhaust dyeing application sequence for polyester is shown in Fig. 16, showing the three main phases of the process including the heating or adsorption phase, the high temperature or diffusion phase, and the clearing phase.

### 5.2.1 Adsorption phase

The heating or adsorption phase is the most critical in determining the levelness of the dyed fibre and it is essential therefore that the heating rate is appropriate to allow controlled adsorption of the dye. Although in the dyeing of polyester, levelling can occur through migration at top dyeing temperature, in rapid dyeing cycles the time at top temperature is minimal and it is even more critical to ensure dye is applied in a uniform manner during the adsorption phase.

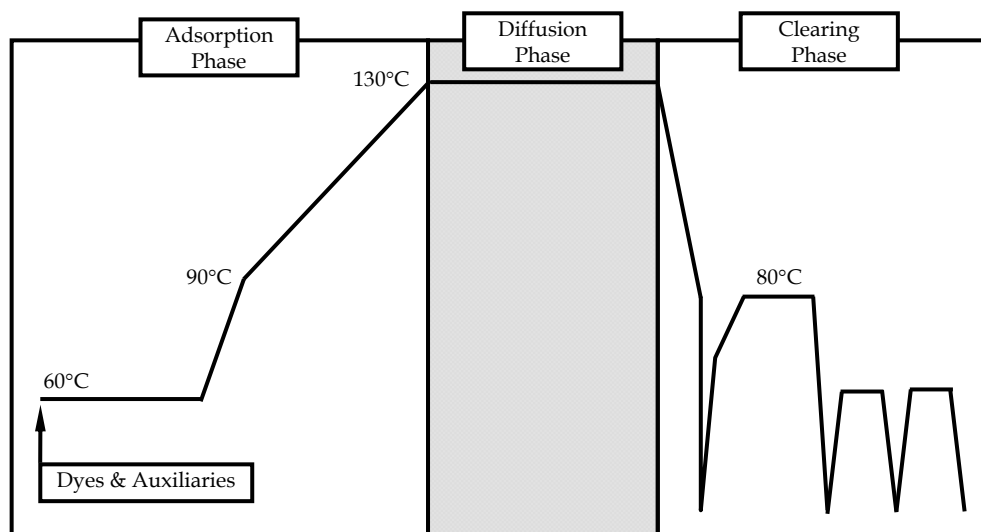


Fig. 16. Phases of exhaust dyeing of polyester.

The adsorption behaviour is strongly influenced by a number of factors, the most important of which are concentration of dye, temperature gradient, fibre type and auxiliary system. The rate of exhaustion of a disperse dye by polyester is controlled by the rate at which the temperature is raised. At some temperature between 80°C and 120°C the dyeing rate for that dye reaches a maximum. The temperature range over which the dyeing rate is at this maximum is known as the 'critical dyeing temperature' (CDT). Slow-diffusing high-energy dyes have a high CDT, whereas more rapidly-diffusing dyes have a lower CDT. Specific values of CDT depend on the rate of temperature rise, dye concentration, liquor flow rate, liquor ratio and the substrate to be dyed. Rapid-dyeing procedures depend on adding the disperse dyes at a temperature just below the CDT and then raising the temperature slowly in the vicinity of the CDT to ensure that the exhaustion rate that just permits level dyeing is not exceeded. The temperature is then raised from just above the CDT to the top dyeing temperature at the maximum rate.

### 5.2.2 Diffusion phase

The dyeing of polyester is often described as a diffusion-controlled process. This is because of the diffusion phases shown in Fig. 16, including convective transfer through the liquor adsorption and molecular diffusion into the fibre, is the rate-determining step (Dawson & Todd, 1979). Where the time needed for the adsorption phase is largely influenced by the machine conditions, in the diffusion phase the time required at top temperature is directly related to the diffusion characteristics of individual dyes and dyeing depth, but generally, the standard time is 10-20 minutes for dyeing up to pale shades, 20-30 minutes for medium shades and 30-35 minutes for deep shades.

In the high temperature phase of the dyeing process, another important property of dyes is migration, or their tendency to level out. This phenomenon can be very important, particularly if dyes have been adsorbed in a non-uniform manner, perhaps due to inadequate liquor circulation or too rapid a heating rate. While the migration properties of disperse dyes may become a key factor if dyes are applied unevenly during the adsorption phase, the key parameter in the diffusion phase is the diffusion rate of the disperse dye.

### 5.2.3 Clearing phase

Because disperse dyes have such limited solubility in water, some particulate disperse dye may still be occluded on fibre surfaces after the dyeing phase is complete (Aspland, 1997). If not removed, this surface contamination can undermine the brightness of shade as well as the wash, sublimation and crock fastness results. Commonly, the dyed polyester is cleared of surface-deposited dye as well as auxiliaries (e.g. carriers, surfactants) by means of treatment with detergent or reductive or oxidative treatments, in order to secure optimum fastness of the dyeing and also to improve the brightness of shade (Burkinshaw, 1995).

The usual treatment carried out, especially in heavy depth, is reduction-clearing, where the dyed fibre is treated in a strong reducing bath, usually made up of sodium dithionite and caustic soda. A treatment for 20 minutes at approximately 70-80°C, is often sufficient to clear the fibre surface, but the ease of removal varies from chromophore to chromophore and dye to dye. This treatment acts to destroy loose azo disperse dye through chemical reduction of the azo link (Fig. 17). Anthraquinone disperse dyes are not fully destroyed by such a treatment but a degree of removal of surface dye is achieved through temporary solubilisation of the disperse dye to the alkali-leuco form. (Aspland, 1997).

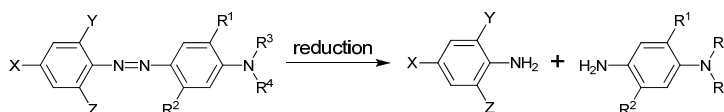


Fig. 17. Chemical reaction during reduction clearing

Research indicates that the polyester dyer will typically reduction-clear in the range of 30-50% of production shades and sometimes an even higher proportion in blend dyeing. Minimizing the need for reduction-clearing can lead to substantial productivity improvements and water and chemical savings as well as a reduction on the effluent load and should be a key objective in implementation of a rapid dyeing approach for polyester.

In the cases of pale and medium-depth dyeings or for those dyes which cannot withstand reduction-clearing, the dye fibre can be given an alkaline scour (Waring & Hallas, 1990); residues of anthraquinone dyes which may remain after reduction-clearing, may be removed using an oxidative treatment (Nunn, 1979).

### 5.3 Thermosol process

Thermosol dyeing process is important continuous process for dyeing polyester and polyester/cellulose fibre mixture with disperse dyes, which is used mainly for wovens and knitted materials (H. K. Rouette, 2000).

A dispersion of the disperse dye 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. Final drying of the padded material takes place using heated cylinders and 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 1-2min. In hot air, as the fabric approaches the maximum temperature, the disperse dyes begin to sublime and the polyester fibres absorb their vapours (A. D. Broadbent, 2001).

Dyes of lower molar mass tend to sublime more readily, but they also suffer from low fastness and poor resistance to heat treatments. Dyes of higher molar mass have better fastness properties but are more difficult to apply. After thermofixation, scouring or even a reduction-clearing treatment is necessary to remove any dye remaining on the fibre surfaces (R. M Christie et al, 2000).

PET seatbelt webbing is typically dyed with disperse dyes using thermosol dyeing processes in which the webbing is dipped continuously into a dye solution and passed through a hot chamber (ca. 220°C) for approximately 2-3 min. The dyestuffs can penetrate the molecular chains of the fibres during their exposure to the hot chamber. This method has some advantages that could avoid a batchwise process (a conventional dyeing method), which is regarded as time-consuming and tedious, and would speed up the dyeing process.

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