ASDC Dyeing of Synthetic Fibres

6.9 Dyes Used – Polyester Fibres

Polyester fibres

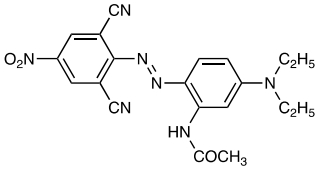
The remarkable global popularity of PES fibres [section 2.1] can be attributed to the facts that the fibre can be produced in a variety of physical forms suitable for different applications, including the commercially very important blending with other types of fibre (eg polycotton), and the generally excellent textile characteristics and high chemical resistance of PES substrates. As discussed in section 3.1, the physical properties of PES fibres (eg degree of crystallinity, orientation, linear density, cross-sectional shape, etc.) vary according on the processing conditions (polymerisation, spinning, drawing, texturising, etc.) used. Thus, the dyeability of different types of PES fibre will also vary considerably for different examples of PES fibres; therefore, the following discussion serves as a general guide to the dyeability of PES fibres.

PES fibres are dyed predominantly using *disperse dyes*, which provide a wide range of hues and display generally very good fastness properties on the fibres, although some dye combinations can display anomalous light fastness to light.

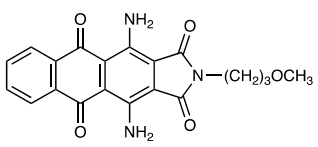
Disperse dyes

A disperse dye is defined as '*a substantially water-insoluble dye having substantivity for one or more hydrophobic fibres, eg cellulose acetate, and usually applied from fine aqueous dispersion*' (61). 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.

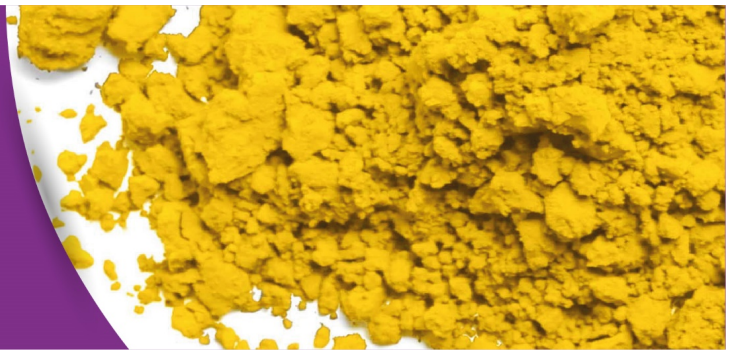
A considerable amount of literature has been published regarding the development, chemistry and application of disperse dyes [see (1) and the references therein].



C.I. Disperse Blue 165



C.I. Disperse Blue 87

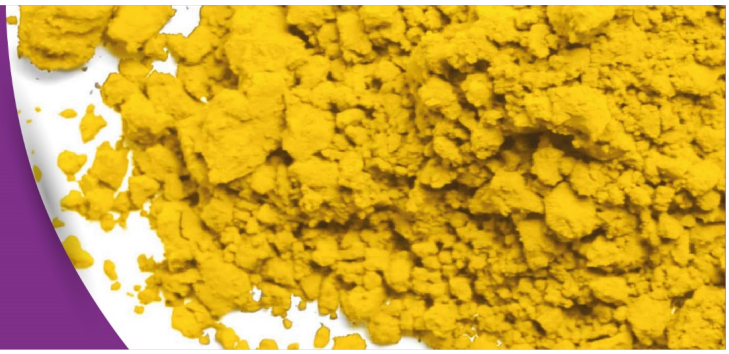


Disperse dyes belong to several chemical classes, predominantly azo (eg C.I. Disperse Blue 165) and anthraquininoid, *AQ,* (eg C.I. Disperse Blue 87). From the viewpoint of their application from aqueous dyebaths, the most significant characteristic of disperse dyes is their very low, but crucially *very important*, aqueous solubility, that enables the dyes to be applied to PES (and other types of fibre) in the form of a *fine aqueous dispersion* in the *presence of dispersing agents*. As the dyes characteristically display very low rates of diffusion within PES fibres at temperatures ≤98°C, commercially acceptable rates of dyeing are achieved using either a dyeing process referred to as *High Temperature* (*HT*) *dyeing* in which the dyes are applied under pressure in the region of 130-140°C or a dyeing process referred to as *carrier dyeing* that utilises fibre *plasticisers* (aka *carriers*) at the commercial boil (98°C). The *non-ionic*, low molar mass dye molecules are *volatile*[1], a feature that is utilised in a dyeing process referred to as *vapour phase dyeing* (aka *Thermosol dyeing*) in which the dyes are applied to PES fibres at ~200°C.

No universal system of classifying disperse dyes has been adopted; in this context, the SDC proposed a series of tests to express the dyeing behaviour of disperse dyes on CA (62), CTA (63) and PES (64) fibres. Dye makers usually classify their disperse dyes according to, for example, sublimation character, diffusional behaviour, fastness properties, etc. A common method of classification is based on the dye's *energy level* (ie *low*, *medium* and *high-energy* dyes) according to which, as the energy level of the disperse dye increases, so molecular size increases and, therefore, volatility decreases (ie sublimation fastness increases) and wet fastness generally increases; high energy dyes are suitable for vapour phase dyeing processes.

The characteristic low aqueous solubility of the dyes, which depends on the physical form of the colorant, accrues from the presence of polar groups (eg –OH, $-NH_2$, C_2H_5OH, etc.) in the dye molecules. The solubility of disperse dyes increases, markedly, with increasing temperature which is of significance for their application to PES fibres under High Temperature, *HT,* dyeing conditions (ie 130-140°C). Dye solubility is also greatly increased in the presence of commercial *dispersing agents*, a characteristic that is utilised in *HT dyeing* processes and which also forms the basis of the *finishing process* that is employed in the manufacture of disperse dyes. Indeed, dispersing agents are a vital component of disperse dyes and are of fundamental importance in the aqueous disperse dyeing of PES fibres.

[1] a *volatile* compound has a high vapor pressure and readily vapourises and moves to the gaseous phase



Briefly, to convert the as-synthesised, *crystalline* disperse dye into the desired commercial product involves *communition*[2], which is commonly achieved by milling an aqueous dye slurry in the presence of a commercial *dispersing agent* (aka *dispersant*). The dispersing agent (eg lignin sulfonates or formaldehyde polycondensates of arylsulfonic acids) expedites particle size reduction, prevents dye particle agglomeration and stabilises the ensuing *dye dispersion*. Although commercial disperse dye samples typically contain large amounts of dispersant (~ 60% by mass), additional dispersing agent (~0.5-2 gl^{-1}) is commonly added to disperse dye dyebaths to maintain *dispersion stability* during aqueous dyeing and promote uniform dyeing.

HT dyeing

In this very popular dyeing process, the dyes are applied at temperatures in the region of 130-140^{o}C to overcome the inherently very low rate of diffusion of the dyes within PES fibres. Because of the high temperatures required for dyeing, the process is energy-intensive and the machines utilised must be able to operate at pressures >1 atmosphere. Typically, dyeing is undertaken at ~60^{o}C in the presence of ~0.5-2 gl^{-1} dispersing agent and 1.5 gl^{-1} non-ionic surfactant to aid dye dispersion and levelling, at pH ~4-4.5 using CH_3COOH[3]; when the temperature reaches 120-140^{o}C, dyeing is continued for 30-60 min, after which time, the temperature is reduced to ~70-85^{o}C to prevent oligomer deposition on the substrate and the fabric is rinsed to remove surplus dye as well as dyeing auxiliaries. The dyeing is finally subjected to a *reduction clearing process* to secure optimum fastness.

During HT dyeing, anionic levelling agents help to solubilise the dye, promote levelling and diffusion within the fibre whilst non-ionic levelling agents increase dye solubility and thereby retard the rate of dyeing; carriers can also be used in HT dyeing to improve dye migration. Small amounts of oligomer migrate to the fibre surface during HT dyeing and transfer to the dyebath. Some oligomers, notably GT_3, can deposit on the fibre during cooling, which impairs both the brilliance and colour strength of dyeings; discharging the dyebath without prior cooling (eg at ~70-85^{o}C) reduces such deposition. Oligomer deposits on machine surfaces can be removed using reduction clearing.

As discussed [section 7.1], because PES microfibres adsorb disperse dyes at a faster rate than their conventional linear density counterparts, dyeing is usually commenced ~10^{o}C lower than that employed

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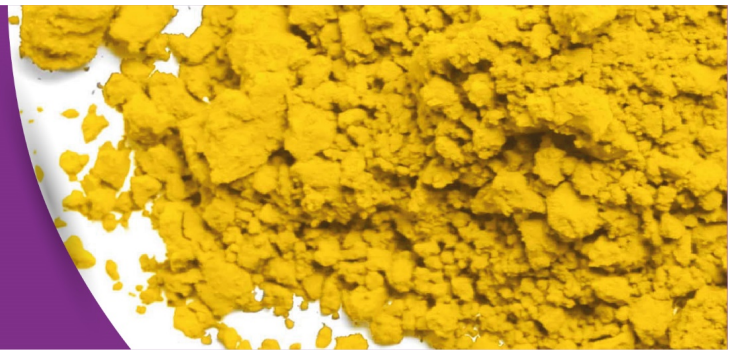
[2] the (average) particle size of the as-synthesised dye solid is reduced to the desired, smaller (average) particle size

[3] acidic conditions are employed as some disperse dyes are unstable under alkaline conditions



for conventional PES, a slower rate of temperature increase upto 120-140°C is used and the holding time at top temperature is extended by ~30 min to expedite dye levelling.

Carrier dyeing

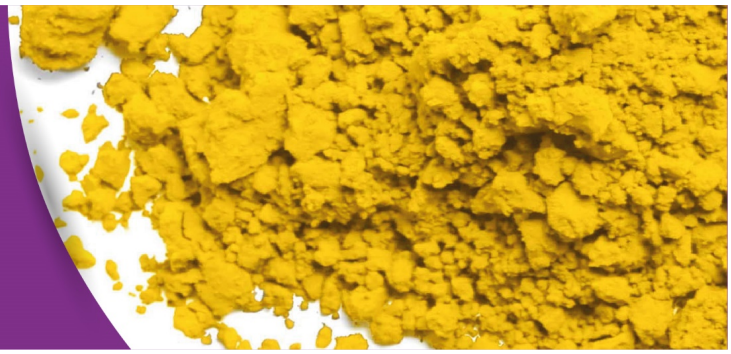
A carrier[4] is *a type of accelerant particularly used in the dyeing or printing of hydrophobic fibres with disperse dyes* (61). Although several theories have been proposed to explain the mechanism by which carriers promote the uptake of disperse dyes on PES fibres, it is generally held that the, characteristically, low molar mass organic compounds, act as *plasticisers*, lowering the T_g of the PES fibre, which increases the amount of free volume available within the polymer, so that the temperature at which the dye molecules can diffuse within the polymer is reduced [see (1)]. Carriers therefore promote dye uptake by increasing the rate of dye diffusion within the substrate at a given temperature; carriers are also used as levelling agents in the HT dyeing of PES fibres. However, because carriers possess several disadvantages (eg malodour, impairment of light fastness, environmental concerns, etc.) the use of carrier dyeing has declined in recent times. During carrier dyeing, levelling agents are not required.

For example, dyeing is undertaken at ~50-60°C in the presence of ~0.5-1 gl^{-1} dispersing agent and carrier (amount used provided by the dye maker), at pH ~5-6 (eg CH_3COONa/CH_3COOH); when the temperature reaches 98°C, dyeing is continued for 30-60 min, after which time, the temperature is reduced to ~85°C to prevent oligomer deposition on the substrate, and the fabric is rinsed to remove surplus dye and dyeing auxiliaries. The dyeing is finally subjected to a reduction clearing process to secure optimum fastness.

Mechanism of aqueous dye transfer

Despite the low aqueous solubility of disperse dyes, the accepted mechanism by which the dyes are adsorbed on PES fibres (as well as other fibres) depends upon their dissolution in the aqueous dyebath [see (1)]. In essence, at the start of dyeing, the majority of the dye is present in the dyebath as *particles* (ie aggregates of dye molecules) which form an aqueous *dye dispersion*; also present in the dyebath is a very small amount of *dissolved* dye molecules that comprise a dilute *aqueous dye solution*. Thus, the initial dyebath contains both *dye particles* that reside within a bulk *dye dis*persion, as well as dissolved *dye molec*ules that constitute a small, but nevertheless very important, dilute *dye solution*. Dissolved dye molecules move from the dilute aqueous dye solution to the PES fibre surface, are adsorbed and then diffuse within the amorphous regions. Dye molecules are then released from the aqueous dye

[4] sometimes referred to as an *accelerant* or *dye accelerant*



dispersion into the dyebath and dissolve, thereby replenishing the small aqueous dye solution with dissolved dye molecules, which can transfer to the fibre surface and become adsorbed. This process of dye molecules from the bulk dispersion dissolving and forming an aqueous dye solution from which dye adsorption occurs, continues until either the dyebath contains no more dye (ie is exhausted) or the fibre is saturated with dye.

It follows, therefore, that the characteristically small aqueous solubility of disperse dyes is of crucial importance in terms of the manner by which the dyes are adsorbed onto PES fibres. Although the above adsorption mechanism was originally developed to describe the application of disperse to CA, it applies to all types of substrate dyed using disperse dyes, including PES, PA, etc.

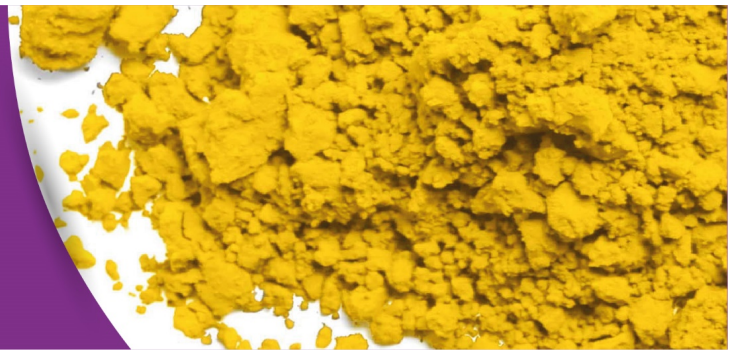
Vapour phase dyeing

In this continuous, pad→dry→bake process, the PES material is impregnated with disperse dyes, dried and then baked for a short time at a high temperature (eg ~5-90 sec at 180-220°C depending on dye and fibre type and heat source (eg cans, hot flue, etc.); dry superheated steam can be used instead of hot air (eg ~175-180ºC, 6-8 min). The dyed material is then rinsed and subjected to reduction clearing.

The process, which offers several advantages over aqueous phase dyeing (eg rapid production, simultaneous heat setting/dyeing), was introduced by Du Pont in 1949 under the trade name *Thermosol*, and is based on the fact that very high rates of dyeing can be achieved at elevated temperatures: for example, a dyeing that may take several hours at 100°C can be secured in <60 mins at 130°C and in 20-30 sec at ~200°C (65). Selected disperse dyes, commonly referred to as *high energy types*, are employed; the dye dispersion contains an anti-*migration* auxiliary (aka *migration inhibitor*) to prevent dye migrating from the interior of the substrate to the peripheral regions during drying. The dyeing process is especially popular for dyeing PES/cotton blends in which the cellulosic component is dyed using vat dyes for example.

Reduction clearing

All dye-fibre systems are subjected to an aqueous treatment, termed *wash-off*, to remove dye molecules which are not physically and/or chemically retained within the substrate, as well as residual dyeing auxiliaries. In the case of dyed PES fibres, because of the disperse dye's low aqueous solubility, aggregates of dye tend to accrue at the surface of the dyed substrate, which reduces the brightness and reduces the wet fastness of the dyeing; also, carriers, oligomers and dispersing agents may also be present at the surface of the dyed PES. The principal aims of wash-off processes are to remove all surface deposits from the dyed material, this being especially important from the viewpoint of the



fastness of the dyeing to wet treatments, such as domestic laundering, since the diffusion of vagrant dye molecules from the dyed material can result in dyeings displaying low fastness.

In the case of PES fibres dyed using disperse dyes, the wash-off process is referred to as *reduction clearing* and, typically, involves treating the dyeings in an aqueous, alkaline solution that contains ~2 gl^{-1} sodium dithionite (aka sodium hydrosulfite; $Na_2S_2O_4$), 1.5 gl^{-1} Na_2CO_3 and 1-2 gl^{-1} non-ionic surfactant at 60-70°C for 15 min. The reduction cleared dyeing is then rinsed in water at 40°C and neutralised using CH_3COOH.

Reduction clearing removes surplus dye and dyeing auxiliaries from the PES material without imparting major changes to the shade of the dyeing, because the pronounced hydrophobicity of the PES substrate prevents the aqueous, alkaline $Na_2S_2O_4$ solution from penetrating the substrate at the temperatures used (~70°C) so that reductive degradation of the disperse dyes occurs preferentially at the fibre surface.

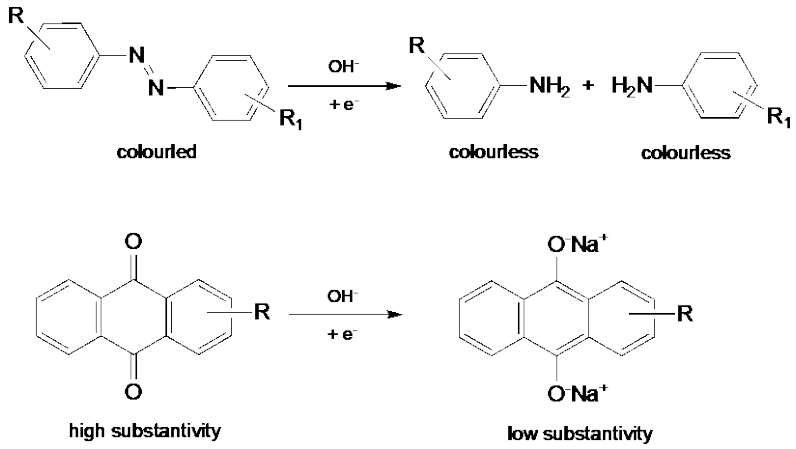
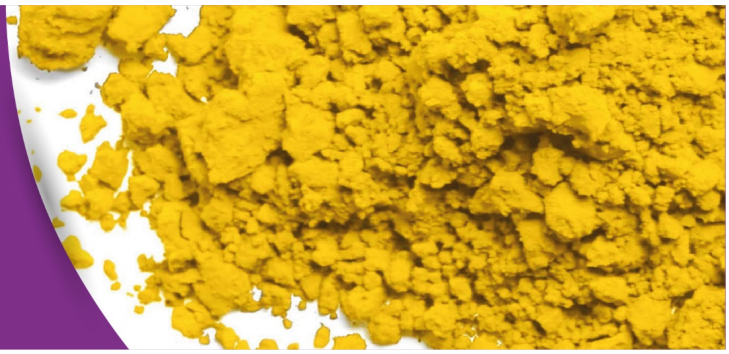


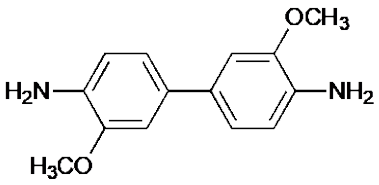
Figure 9 effect of reduction clearing on azo and AQ disperse dyes

However, reduction clearing suffers from several disadvantages insofar as the highly alkaline wastewater contains not only the strong reducing agent $Na_2S_2O_4$ but also residual dye components, as reduction cleaves the azo bond in azo dyes, generating potentially harmful colourless aromatic amino compounds and converts AQ disperse dyes to the virtually colourless, water-soluble, low substantivity, ionised form of the dye (Figure 9).

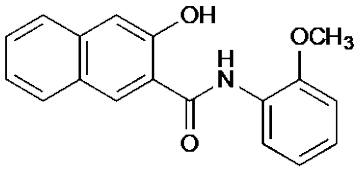


Azoic colorants

An azoic colorant is an insoluble azo compound that is formed in situ within the textile substrate by the reaction between an azoic diazo component, as exemplified by C.I. Azoic Diazo Component 48 and an azoic coupling component, such as C.I. Coupling Component 20; nowadays, azoic colorants are mostly used on cotton.



C.I Azoic Diazo Component Blue 48



C.I. Azoic Coupling Component 20

In the case of PES fibres, the use of azoic colorants is restricted to black shades employing diazotised and developed black disperse dyes (9) [see section 9.4.2].