2.2.3 Alkaline pretreatment for weight reduction

Alkaline pretreatment with NaOH has been used for a number of years to achieve a weight reduction of 10–15%. A finer yarn count results in an improved handle. Alkalising is carried out under HT conditions. The degree of surface etching or removal depends on the concentration of NaOH used, the temperature and the duration of treatment.

Normally, polyester fibre is dyed in an acid medium. A thorough removal of alkali by rinsing, and acidifying to neutralise, is necessary. This step can be omitted, with a saving of time and processing cost, if the alkaline HT process developed by DyStar is employed [11].

2.2.4 Heat setting

Heat setting of the fibre serves to stabilise polyester fabrics. It ensures that the piece goods retain their shape in the processing stages following heat setting and in future use. For many types of structures, and in many dyeing machines, heat setting prior to dyeing can be omitted. In this case, heat setting is carried out after dyeing in the drying and finishing stage.

The heat-setting conditions are governed by the processing history, type of polyester fibre and the type of piece goods. The following can serve as guide conditions.

(1) Woven and knit goods of textured polyester filament: 170–195 °C.
(2) Fabrics of polyester filament: 185–220 °C.
(3) Blends of polyester and cellulose fibres: 190–210 °C.

The contact time depends on the weight of the fabric and the type of heat-setting equipment used.

Heat setting before dyeing has to be carefully controlled to avoid problems with shade variations during dyeing. Small temperature differentials can often produce large shade changes from edge to centre – for example, when dyeing piece goods.

Pre-setting has a negative effect on dye yield. Post-setting, however, generally adversely affects fastness. Changes of shade can also occur, especially in cases of 'ring dyeing'. This is where dye has not diffused into the inner core of the filaments. There is usually good correlation between sublimation-fastness of disperse dyes and the effect of heat-setting conditions. Higher molecular weight disperse dyes normally have greater sublimation-fastness and, therefore, are more resistant to the effect of post-setting.

2.3 DISPERSE DYES

2.3.1 Chemistry of dyes

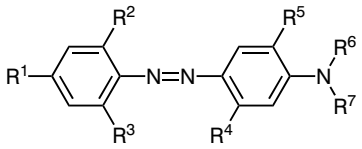
Polyester is almost invariably dyed with disperse dyes. These hydrophobic dyes were originally

developed when cellulose acetate and triacetate were found to be almost undyeable with the hydrophilic dyes needed for natural fibres.

With a worldwide growth rate of polyester of over 4% per year, it is not surprising that the chemistry of disperse dyes has received, and continues to receive, a great deal of attention. The chemistry of the various categories of dyes for different fibres is very similar because the chromophores and auxochromes used are those which are able to create a particular hue, regardless of the substrate. Much of the difference comes in the auxochrome responsible for solubility, in the case of hydrophilic fibres, and the lack of water-solubilising groups, in the case of hydrophobic fibres. An excellent review by Shore can be found in Chapter 1 of *Colorants and Auxiliaries* [12].

Azo dyes

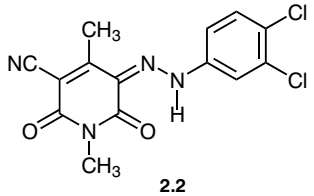
This is the largest class of disperse dyes, providing approximately 60% of commercial dyes. The chemistry incorporates the azo chromophore between two aromatic rings. The rings are further substituted with electron-attracting and electron-withdrawing groups called auxochromes. The major hues are yellow, orange and red; however, violets, blues and blacks are well known. The general formula is as shown in Structure **2.1**, where R^1, R^2, R^3 = H or an electron-withdrawing group (for example, $–NO_2$, –CN, halo or alkoxycarbonyl, although weakly electron-donating groups are occasionally encountered; one example is where R^1 is a methyl group, as in CI Disperse Red 343), R^4, R^5 = H or an electron-donating group (for example, OCH_3) and R^6, R^7 = H or alkyl or further substitution.



2.1

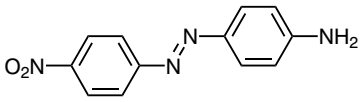
Note that the effect of substitution in the diazo component (on the left) is always one of net electron withdrawal. Similarly, the net electronic effect of substituents in the coupling component (on the right) is always one of electron donation. The coupling component needs to be sufficiently electron-rich to undergo electrophilic attack by the aryl diazonium salt.

There are also several popular dyes – for example, CI Disperse Yellows 241 (**2.2**) and 242 – where substitution in the 3-position of the diazo component in Structure **2.1** is also found.



2.2

The simplest of these structures, and among the earliest disperse dyes to be synthesised, was CI Disperse Orange 3 (**2.3**). However, the physical properties of such a small dye molecule, developed for dyeing cellulose acetate, gave inadequate fastness properties for dyed polyester. Structure **2.4** is a scarlet dye and is known to give improved light-fastness. In the late 1960s and early 1970s, bright blue monoazo disperse dyes began to appear and were offered as replacements for anthraquinone-based blues. Typical of these dyes is CI Disperse Blue 165 (**2.5**).



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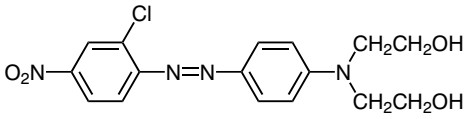

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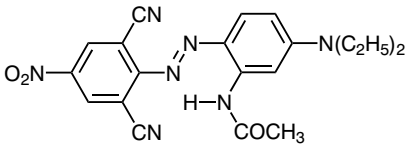
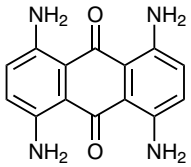


2.5

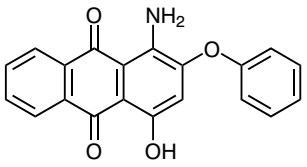
Anthraquinone dyes

This class is second largest of all disperse dyes, and has been very important in the past. However, there has been much effort over recent years to replace these chromophorically weak dyes with stronger, and therefore more economic, types such as azo thiophenes. Anthraquinone dyes were developed in the 1920s for the coloration of cellulose acetate. As new synthetic fibres such as nylon, cellulose triacetate and polyester were developed, chemists turned to this chemistry for reliable commercial products. Most hues are in the pink, red, violet and blue range. Once again the earliest dyes, such as CI Disperse Blue 1 (**2.6**), which had been developed for cellulose acetate, gave inadequate fastness properties.

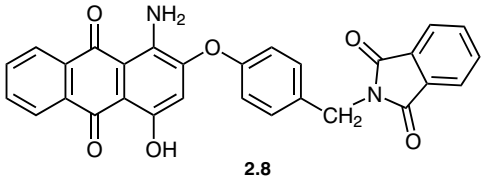


2.6

Diffusion of relatively low molecular weight dyes is quite rapid. Consequently, diffusion out of the polymer is also high and therefore wash-fastness is generally poor. Additional substitutions to the central chromophore led to dyes such as CI Disperse Red 60 (**2.7**) with moderate sublimation-fastness. This characteristic makes it the most important red dye for transfer printing [13]. Improved light-fastness is achieved by adding additional molecular weight to the



2.7



2.8

side-chain in the case of the modification to CI Disperse Red 60 (**2.8**). CI Disperse Red 263 has a similar structure.

The anthraquinone disperse dyes developed over the years have met the demands of commerce by providing:

(1) bright shades, especially blues and reds;
(2) very good light-fastness;
(3) good level dyeing;
(4) good coverage of barré;
(5) good reproducibility.

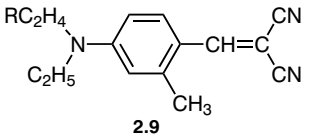
Anthraquinone disperse dyes have been found to be extremely useful in dyeing at atmospheric pressure. It is common practice to employ carriers to increase dyestuff yield in low-temperature processes. Carrier dyeing at low temperature is an important process in the dyeing of wool/polyester blends. Further increases in dyestuff yield can be achieved by including a wool protective agent and increasing the temperature. In general, as a class, anthraquinone disperse dyes display the following deficiencies:

(1) they are tinctorially weak, requiring large quantities for dark shades;
(2) they exhibit poor wet-fastness;
(3) they are expensive (though, recently, cheaper dyes manufactured in China have become available);
(4) there have been environmental problems in manufacture.

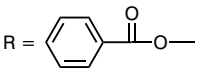
The environmental problems were related to the mercury catalyst used by many manufacturers. However, new processes in Japan have led to mercury-free catalysts, and these are now commonplace.

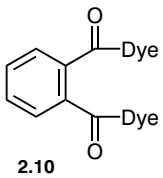
Styryl (methine) dyes

This small class of dyes (approximately 2% of commercial dyes) was developed to provide brilliant greenish-yellow hues. The simplest structure is depicted in Structure **2.9** with the R group as illustrated. For additional fastness, two of these chromophores can be coupled through the pendent ring (**2.10**).



2.9

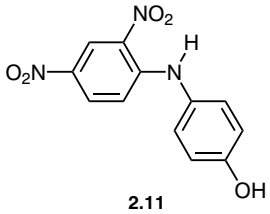




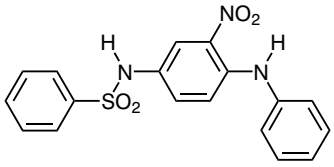
2.10

Nitrodiphenylamine dyes

A relatively small group of duller yellow and orange-yellow dyes are formed with this chromophore – for example, CI Disperse Yellow 1 (**2.11**). Again, fastness for the smallest structures is inadequate for polyester but is suitable for cellulose acetate [13]. A larger workhorse disperse yellow is formed by making minor structural changes to give CI Disperse Yellow 42 (**2.12**), which has improved light-fastness, though its wet-fastness properties remain poor.



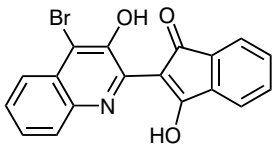
2.11



2.12

Heterocyclic ring structure dyes

Heterocyclic chromophores such as quinophthalone produce bright colours, especially the greenish-yellow shown in Structure **2.13**. The brominated version is well known as CI Disperse Yellow 64. The unbrominated version has lower fastness but is well known as CI Disperse Yellow 54 (**2.14**).



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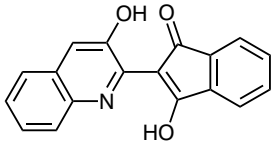
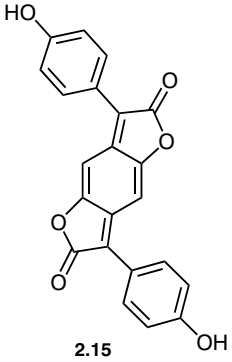


2.14

Benzodifuranone chromophores

The fastness inadequacies of the bright red anthraquinone dyes – for example, CI Disperse Red 60 (**2.7**) – led ICI to follow up on research released in 1960 by Junek [14], which reported the formation of novel red pentacene quinone from the reaction of benzoquinone with cyanoacetic acid. The proposed dye structure could not be confirmed. Further work by Greenhalgh at ICI

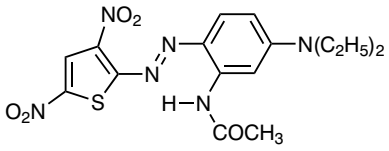
revealed the structure to be a benzodifuranone dye. This dye is of no commercial value but further work on this chromogenic system led to a series of very bright red dyes, Dispersol Red C-BN and Brilliant Scarlet D-SF. The generalised structure for this class of dye is shown below (**2.15**).



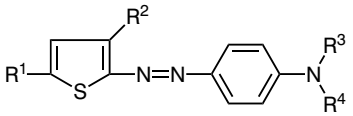
2.15

Thiophene type

Monoazo thiophene dyes were introduced in the mid 1970s (CI Disperse Blues 284 and 295, and CI Disperse Green 9 (**2.16**)), and other blue thiophene dyes followed later. In the mid 1980s disazo thiophene dyes were also marketed. A typical monoazo thiophene dye structure is shown below (**2.17**), where R^1 = an electron-withdrawing group (for example, $–NO_2$), R^2 = an electron-withdrawing group (for example, cyano, nitro or alkoxycarbonyl), R^3, R^4 = H or alkyl or alkyl ether substituent.



2.16



2.17

These dyes offer:

(1) high tinctorial strength;
(2) brilliant blues;
(3) high fastness relative to anthraquinone dyes.

2.3.2 Classification for use on polyester

The commercial offering of a typical dyestuff manufacturer will cover the range given in Table 2.3.

2.3.3 Formulation of disperse dyes

There is often a mistaken belief by users that dyes from different manufacturers with the same Colour Index number are identical and can be used interchangeably. This is not true. Glover

Table 2.3 Chromophores typically present in colorants of various hues

Hue	Typical chromophore
Brilliant yellow	Methine; Coumarin derivative; Pyridone
Yellow	Nitrodiphenylamine; Heterocyclic; Azo with pyridone couplers
Orange	Azo
Red	Azo; Anthraquinone; Benzodifuranone
Pink	Anthraquinone
Violet	Azo; Anthraquinone
Blue	Azo; Anthraquinone; Thiophene
Black	Azo

and coworkers point out that the coloured species may be as little as 10% of the actual commercial product sold [15]. The balance of ingredients is loosely classified as 'formulating agents'. The AATCC's annual Buyer's Guide issued in July each year contains the following statement: *'The CI Generic Name defines the essential colorant only. Commercial preparations in each CI Generic Name may not have identical application, fastness or 'Ecotex' properties; check with the individual manufacturer'* [16]. Any organic chemist familiar with synthesis knows that the isomers obtained by various commercial synthesis routes will yield different products; rigorous process control is essential to assure reproducibility. Manufacturers also blend to assure constant products. Having said all of the above, these very same companies will claim their product is the same as that offered by a competitor.

Glover and coworkers also point out that the above-mentioned *'formulating agents are important because they are needed to convert the virtually insoluble dye into a product which can be evenly applied to the polyester fibre from a hostile aqueous medium. At the high temperatures needed for adequate penetration into the fibre, part of the formulation must provide dispersion stability. A poor choice of these agents can lead to fibre staining in blends, lower rub-fastness, excess foaming during the dyeing process, and interaction with other dyebath ingredients'* [15].

Lastly, in more and more locations worldwide, the ingredients must be ecologically friendly. In a typical exhaust dyeing, virtually all of the dye is exhausted from the bath and virtually all of the auxiliary chemicals are left behind. Many suppliers must now provide information on aquatic toxicity to fish and microorganisms, and biodegradability. In the United States, the Environmental Protection Agency mandates Material Safety Data Sheets (MSDS), which must accompany all chemical shipments and must include biological toxicity information. In Germany, Sicherheitsdatenblatten (Safety Data Sheets) mandated by the Bundesminister für Arbeit und Sozialordnung (Federal Ministry for Work and Social Order) serve the same purpose. The same format is used across the entire European Community.

2.3.4 Preparation of the dye liquor

Commercial dyestuffs are supplied as dedusted powders, pourable granules or liquids. The granules are specially formulated with dispersing and stabilising agents in order to minimise

dusting or fragmentation of these granules into finer powders, which take to the air and contaminate the colour kitchen and its surroundings. Because of health and safety considerations, larger dyehouses have tried to use liquid dyes when and wherever possible. These dyes can be handled easily by automated dispensing systems.

Granules are dispersed at 20–30 °C into 5–15 parts of softened water per part of dye. Liquid formulations can be added directly into the mix tank or diluted with soft water at a maximum temperature of 50 °C. Higher temperatures and the use of high-speed stirrers are not recommended since they can lead to agglomeration of dyes and specking of intense colour on the goods. Temperatures below 20 °C result in unsatisfactory dispersion of the granules.

2.3.5 Dispersing agents

Dispersing agents are used in the manufacture and application of insoluble dyes. The importance of dispersing agents extends to each and every part of dye preparation and dyeing. After the dyestuff is synthesised in the reactor and the solid particles filtered, there are at least two methods for processing the press cake. More often than not it is fluidised in water with dispersing agent and then milled (ground) to achieve a uniform particle size. It is then converted to a liquid or powder using other additives.

Alternatively, the press cake is dried and the resulting dye ground to a uniform particle size distribution, which should be uni-modal rather than having several distributions of fine and coarse particles. When the particles are dispersed in water, dispersing agents play an important role in achieving and maintaining narrow, uni-modal particle size distributions at room and elevated temperatures [16].

The specific requirements differ for each of the distinct dye processing procedures and end-uses. For example, the reduction of dye particle size during cake grinding does not require the dispersing agent to adsorb as strongly to the particles as is required when batch dyeing. Dilling and Eicke found that medium-sulphonated lignin sulphonates work better for grinding, even though they adsorb less than the low-sulphonated varieties [17]. These anionic polymers are derived from the Kraft wood-pulping process. There is no known structure [18]. The repulsive forces of the sulphonate groups prevented dye particle interaction during grinding. Steric hindrance and non-adsorbed dispersants were also important in preventing agglomeration.

During dyestuff storage, more dispersant is required to prevent agglomeration than during grinding. System pH, crystal size and electrolyte concentration must also be controlled. The optimum pH for storage is near 7; higher pH allows agglomeration due to lower dispersing agent concentration at the dye–water interface. As the pH increases, phenolic and carboxylic acid groups dissociate and give less adsorption capability. Conversely, low pH causes the dispersants to be attracted to one another, their size grows and the particles are left unprotected. Low pH also means the sulphonate groups on the lignin sulphonate give lower water solubility and increase their mutual attraction leading to flocculation.

As crystals grow, stability decreases, much like sugar crystallises from a saturated, hot water solution. Adsorption of surfactants on dye crystals can alter the surface enough to prevent

access by the lignin sulphonate dispersing agent. Without this protection, the crystals grow by a phenomenon known as 'Ostwald ripening', caused by differences in surface energy. Large particles consume small particles. The extent of this growth depends on the specific chemical and physical nature of the dyestuff but is largely related to the particle size differences.

Storage stability is negatively affected by concentrations of free electrolyte above 5%. Extra electrolyte results in higher viscosity as the thickness of the protective dispersing layer is reduced and these particles come closer together. Hydration of the electrolyte also increases viscosity. The low degree of sulphonation of some lignin sulphonates allows them to be highly affected by electrolyte concentration. Gelling is a common phenomenon at high-electrolyte concentrations.

Dyeing requires strong adsorption and full coverage of the dispersed particles. Between 20% and 60% of every commercial disperse dye sold consists of dispersing agents [19]. Additional dispersing agents are also added to dyebaths to ensure good operating conditions. A full discussion of dispersing agents is given by Baldwinson [18].

2.3.6 Commercial disperse dyes for polyester

The polyester fibre is extremely hydrophobic; indeed, it is one of the most hydrophobic fibres, with a moisture regain of approximately 0.4% at standard conditions of 20 °C and 65% relative humidity. Dyes developed for the dyeing of the first hydrophobic fibres – cellulose acetate and cellulose triacetate – were modified to adapt to the new polyester fibre upon its development in the 1940s. The dye molecule could have no ionisable or dissociable groups, nor any other groups that could promote water-solubility. These dyes would prove to dissolve only very sparingly in very hot water.

In order to promote dyeing from an aqueous bath, the dye press cake had to be ground or ball-milled to a fine particle size (normally below 1×10^{-6} m) and very carefully controlled from batch to batch. Anionic surfactants, typically lignin sulphonates produced as a by-product of the Kraft paper-making process, are used extensively. These large surfactant molecules, which are several orders of magnitude larger than any disperse dye molecule, adhere to and encapsulate the large dye pigment particle and form a stable dispersion [20]. This dispersion must withstand a wide range of temperatures and allow the gradual dissolution of the individual dye molecules from the larger pigment particle. The system chosen for the preparation of the dispersion must be compatible with all dyes in the product line.

Variations can occur from manufacturer to manufacturer. Dyes from different sources that have the same CI number may behave differently and may not dye in the same manner. Formulations are being changed today in order to deliver better environmental conditions, such as reduced Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD).

When combining dyes to form a typical trichromatic combination, one must be aware that dyes have different affinities, different molecular structures and different diffusivities. All of these affect the time of dyeing and must be taken into consideration when planning which dyes should be used in combination for a particular application.

2.4 EXHAUST DYEING

2.4.1 Practical aspects of exhaust dyeing

The development of polyester as a major textile fibre was initially held up due to the poor uptake of disperse dyes by poly(ethylene terephthalate) at 100 °C. As a result, carriers were employed (Section 2.4.4) but these were strong-smelling and toxic. It was only when high-temperature, pressurised dyeing machines were introduced, thus rendering the use of carriers unnecessary, that polyester was able to challenge nylon as the premier synthetic fibre.

Initially, high-pressure winches and beam dyeing machines were used, but when jet dyeing machines were introduced these rapidly gained prominence. There are several different types of jet machine: long style, compact, water driven and air driven. White [21], in his review on jet dyeing, lists 43 companies offering jet machines at the 1995 ITMA show. The choice of machine depends on the fabric structure and the final appearance and handle required.

A typical dyeing cycle is illustrated in Figure 2.2. The dyebath is set with dispersing agent and the sieved dye slurry added, the pH having first been adjusted to 4–4.5 with acetic acid. The acidic conditions are necessary as some disperse dyes are unstable under alkaline conditions. The temperature is then raised at 1–2 °C min^{-1}. After dyeing at 125–130 °C for 45–90 minutes, depending on the shade, the bath can be cooled down to 90 °C for shade checking. After making shading additions as necessary, the temperature is raised again to 125–130 °C and the dyeing continued for a further 30 minutes. If the sampling device on the machine is reliable, it may be possible to avoid cooling before sampling. When the shade is satisfactory the bath is cooled to 70 °C before dropping the bath. Rinsing and reduction clearing follows (Section 2.4.7).

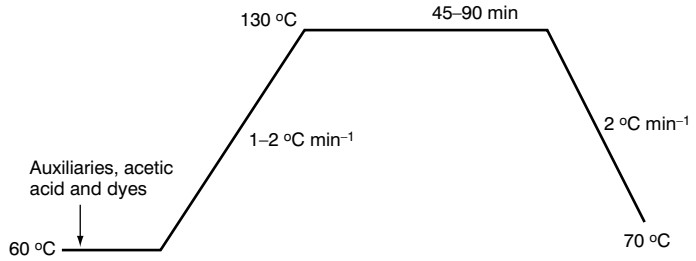


Figure 2.2 Typical 'right first time' dyeing cycle for PET

2.4.2 Dyeing mechanism and approach to equilibrium

As dye molecules dissolve in the surrounding liquor, it is assumed that they behave as single molecules and move quickly away from the large pigment particle toward the fibre with the aid of bath circulation, or return to the same or another large particle. The dyes approach an equilibrium distribution that is generally described by the Nernst isotherm [22]. Dyeing conditions should be adjusted to ensure that the supply of dye is adequate to saturate the fibre surface. The outer layer becomes saturated as diffusion is the limiting step. Since there are no

charged sites in the normal PET fibre, there can be no site saturation as there can be with other ionic dye systems and ionisable fibres.

Each dye molecule is believed to move independently of the other molecules once on the fibre surface and within the fibre unless affected by certain auxiliary chemicals such as carriers, which promote migration. In the dye liquor itself, different dispersing agents can have an effect and must be considered when combining dyes from different manufacturers [23]. In normal commercial dyeings, there is an approach to an equilibrium distribution of dye throughout the fibre. However, true equilibrium is not commercially justified. Beckmann and others feel an approach to approximately 90% is sufficient [23]. Exhaustion from the bath will be higher than 90% but the internal diffusion will only approximate this figure.

2.4.3 Dyeing theory

The mechanism of dyeing, or the steps involved, are as follows.

(1) The dye is dispersed in powder form into the dye liquor or the liquid dispersion is diluted. A very small portion dissolves; the remainder stays in particle form. No equilibrium is established due to crystal growth and aggregation between the smaller particles and larger particles. These surface-tension-related forces are known as Ostwald ripening and describe the loss of smaller particles due to the growth of the large particles.

(2) As the dye arrives at the fibre surface, part is adsorbed and part returns to the liquor. This partition depends on a number of parameters including, among other things, the degree of dispersion, temperature, auxiliaries used and fibre crystallinity.

(3) Dye molecules diffuse into the fibre following the most open structural voids (amorphous areas or volumes) while avoiding the more ordered crystalline regions.

(4) Dyeing is said to be complete when the surface concentration is depleted and the diffusion front moves into the interior such that it fills more than one third of the fibre radius. Shallow penetration is referred to as 'ring dyeing' – an effect to be avoided since surface abrasion will eventually uncover the undyed fibre regions in the normal course of wear. The uncovering gives what is called a 'frosty' appearance.

The first two of these steps are complex and not fully investigated. However, the rate-limiting step is the diffusion step described by Fick's first law of diffusion (Eqn 2.1):

$$-\frac{dC}{dt} = D\ \frac{d^2C}{dx^2} \tag{2.1}$$

where C = dye concentration in the bath
D = the dye diffusivity
x = distance
t = time

Beckmann specifies a concentration C_s that is different from the real surface concentration C, and relative values of the diffusivity to achieve practical results [23].

At low temperature, the dense crystalline/amorphous structure prevents penetration of the dye molecules. As the glass transition temperature, T_g (approximately 85 °C), is approached, dyeing begins. Chemical auxiliaries, or carriers, help lower the T_g and dyeing begins at lower temperatures. Diffusion increases and becomes important in the range 80–85 °C, following the Arrhenius equation (Eqn 2.2) below, with an activation energy E of 40–50 kcal mol^{-1} °C^{-1} for normal PET fibres. The dyeing rate can be described by:

$$v(T_{abs}) = v_0 \times \exp\left(-\frac{E}{RT_{abs}}\right) \tag{2.2}$$

where v = rate of dyeing
v_0 = initial rate of dyeing
E = activation energy of the dyeing
R = universal gas constant
T_{abs} = absolute temperature

The results of these investigations showed that an increase of 5 °C doubles the dyeing rate and reduces the diffusion by half. This is independent of fibre type, dye and dye concentration and independent of the use of carrier.

In a case study, where dyeing is level from the start of the process [23], dyeing follows a linear time–temperature relationship in which, above the starting temperature T_{st}, dye exhausts at a rate r = 4% °C^{-1}, giving a critical temperature range, ΔT_{crit}, of 25 °C (see Figure 2.3). Since dyeing begins at T_g > 85 °C, the temperature range is 85–110 °C. Practical dyeing times are achieved only when T > 110 °C or if carriers are used to reduce the effective temperature.

The rules for T_{st} are as follows.

(1) Each dye in a bath has its own T_{st} and position of ΔT_{crit} independent of other dyes present (Figure 2.3b).
(2) T_{st} depends on the dyeing properties of the dye – it increases with increasing amounts of dye present (Figure 2.3a) and depends on fibre orientation, crystallinity and V value (a fibre dyeing rate constant).
(3) When combinations are dyed, the T_{st} of each dye may differ; the ΔT_{crit} of the dyes may overlap or may exceed 25 °C (Figure 2.3b).

For a constant temperature, the dye concentration on the fibre, C_F, builds up according to the $\sqrt{t}$ law (Eqn 2.3).

$$C_F(t) = k\sqrt{(Dt)} \tag{2.3}$$

where k is a constant.

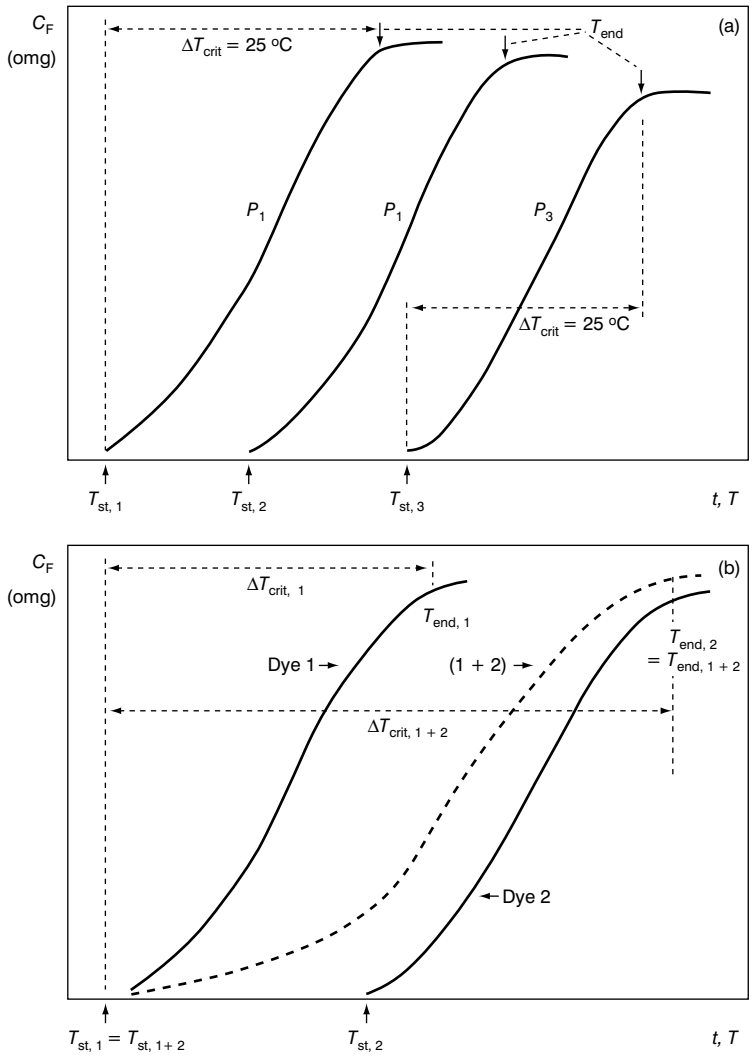


Figure 2.3 Exhaustion curves for disperse dyes, dyed with time-linear increase of temperature: (a) single dye in three different depths P; the higher P, the higher is T_{st}; the size of ΔT_{crit} remains unchanged, *c*. 25 °C, but its position shifts with P; (b) two dyes in combination; the dyes do not significantly influence one another, but a larger ΔT_{crit} results. C_F represents dye concentration on the fibre (from [23] p22)

This relationship holds below 70% exhaustion; above that the build-up is progressively slower. The constant mainly represents the effective dye concentration on the fibre surface (which in turn is related to, among other things, the solubility of the dye in the liquor). Eqn 2.3 means the rate of dyeing slows during dyeing unless T is increased; temperature should be increased at least until exhaustion is complete (to $T > T_{end}$). These relationships can be used to set up a

time–temperature program such as the Compudye System (DyStar), which quantifies and organises these parameters into a systematic dyeing procedure. This program takes into account:

(1) the dyeing characteristics of the individual dyestuffs;
(2) the influence of levelling agents, carriers and retarders;
(3) the dyeing properties of the fibres;
(4) the type of equipment (package, beam or jet dyeing machine);
(5) the dyeing conditions (minimum temperature, liquor ratio, liquor circulation or running properties of the goods).

The calculations can be adjusted to the requirements of individual dyehouses by empirical correction factors.

2.4.4 Carriers

As discussed in the previous section, PET should normally be dyed above 110 °C, in the HT range, to obtain commercially acceptable exhaustion and dye diffusion rate. This is true for pale shades as well as deep shades. HT dyeing conditions, however, are not always feasible, especially for PET/wool blends, since wool can easily be damaged above 100 °C. A carrier or auxiliary chemical is used to lower the T_g and the T_{st} so dyeing is commercially feasible below 110 °C. For a given temperature, these carriers increase the rate of dyeing and reduce the time needed for penetration and migration. In this case, they can be classified as dyeing 'accelerators'.

Carriers must be similar in hydrophobicity to the PET fibre; they are applied from emulsions or dispersions. As the concentration of carrier inside the fibre increases, acceleration occurs as well. Roughly speaking:

(1) at the same concentration within the fibre, all carriers have the same effect; differences in the performance of carriers result from differing exhaustion properties (temperature range, affinity and behavior of the dispersion or emulsion) – good carriers exhaust at lower temperatures than the dye;
(2) carriers lower T_{end} and T_{st}, resulting in a shift of the position but not the size of ΔT_{crit}.

An acceleration factor, a, has been defined (Eqn 2.4) as:

$$a = \frac{\text{rate of dyeing with carrier}}{\text{rate of dyeing without carrier}} \tag{2.4}$$

where a depends on the concentration of carrier in the fibre and not in the liquor. It does not depend on the dyes used or on their concentration. In the HT range, a decreases as temperature increases. At normal jet dyeing temperatures of 130 °C and above, commercial dyeings take place without the use of carrier.

The carrier that remains in the dyebath after dyeing and the dispersing agents or emulsifiers

in the carrier formulation lower the final exhaustion equilibrium (the colour yield). Selection of the proper carrier minimises this effect. As a positive effect, carriers improve migration of dyes.

Carriers do not promote levelness in the exhaustion phase of dyeing – they accelerate the migration (higher mobility, more dye in the bath) and consequently, can improve levelness in the final stages of dyeing. However, when there are differences in fibre structure and differences in diffusion, they can accentuate unlevelness. Where dyes penetrate more rapidly, the initial unlevelness becomes worse. Such differences often show up as alternating light and dark streaks called 'barré'. In cases where there is a risk of this effect, carriers should be added to the dye liquor after most of the dye has been exhausted.

Depending on the dyeing process, carriers can have unfavourable side effects. When dyeing blends, there may be staining of the other fibre. Other effects, such as odour, aquatic toxicity, lowering the light-fastness and steam volatility, have caused some products to be removed from the market. Residual carrier must be removed from the fibre, usually during drying following dyeing. The total amount of carrier is kept as low as possible, and it is used only when absolutely necessary.

Several important commercial carriers are in the following chemical families:

(1) phenols – for example, ortho-phenyl phenol, biphenyl;
(2) aromatic esters – for example, butyl benzoate;
(3) phenyl ethers;
(4) cresotic acid esters;
(5) mixtures of the above.

Chlorinated carriers such as dichlorobenzene and, lately, phenols have been removed from the marketplace in most developed countries due to aquatic toxicity.

Thus far, no ideal carrier has been identified. The trade-offs are cost and performance and aquatic toxicity.

The following standard recipe and dyeing procedure can be used for dyeing polyester at the boil.

(1) Treat for 10–15 minutes at 60 °C with 3–6% butyl benzoate and biphenyl (3% for light shades) *x*% disperse dye.
(2) Adjust the pH to 4.5–5 with acetic acid and sodium acetate as buffer. Bring to the boil within 30–40 minutes and dye for 60–120 minutes according to the depth of shade.

A reductive clear of polyester or polyester/cellulose piece goods is carried out as described in Section 2.4.7, although the following may also be used:

(1) 2.0% non-ionic levelling agent;
(2) 0.5 ml l^{-1} acetic acid 60% for 20 minutes at 90 °C.

2.4.5 Microfibres and fine polyester fibres

In the late 1980s and early 1990s, fabrics comprising of small denier fibres (0.5–1.0 denier per

filament) called 'microfibres' or 'microdenier fibres' created quite a sensation in Western Europe and the USA, after having caught the imagination of the Japanese market (Table 2.4) [26]. Major fibre manufacturers felt that market share would surpass 50% of the total polyester fibre market in the USA within the first five years, or shortly thereafter. This forecast was overly ambitious for a number of reasons, including high manufacturing cost, which the consumer did not readily accept, and poor colour-fastness not normally associated with early generation larger denier polyester.

Table 2.4 Microfibre in Europe and the US [26]

Maker	Brand name	Denier per filament
Hoechst	Trevira Finesse	0.63
	Micronesse	
North German Fabric Company	Avitron	
	Filafic HM	0.5
Monte Fibre	Terital	
Rhone Poulenc	Setila	
	Microbrin	0.5
Akzo	Diolen	
	Mico	0.63–0.73
Italy (SNIA)	Micrell	
	Val Lesina	0.37
DuPont	Micromattique	0.7
Fiber Industries	Micro Spun	0.5

Meanwhile in Japan the technology had been advancing for a number of years with the development of synthetic leather and suede based on microdenier fibres. Also, a new generation of polyester filament woven fabrics called 'Shin-gosen' were developed in the latter part of the 1980s. Although partially based on a fine denier polyester, the Shin-gosen went much further in blending modified polymers, modified cross-sections, fineness and finishing to achieve several sub-categories of fabrics which were generally categorised by their touch:

(1) worsted wool touch;
(2) rayon touch;
(3) silky touch;
(4) peach-skin touch.

The latter comprised several sub-groups, namely the soft touch, wet touch, micro-powder touch, smoky touch and rose petal touch. The denier range for these sub-groups today ranges from 0.01–0.2 denier. Along with the development of these special fibres, new spinning, weaving and dyeing technology was needed. Blends with Lycra are also gaining in importance.

The very fine denier fibres developed around the world have found special textile uses due to their unique characteristics. The fine denier allows manufacture of water-repellent,

breathable woven fabrics for sportswear; the special peach-skin and silky touch 'Shin-gosen' have found a special market in Japanese women's wear. These fine denier fibres have several problems for the dyer and finisher [26], including:

(1) reduction of the apparent depth of shade due to increased light scattering;
(2) reduction in fastness due to increased influence of light and oxidation;
(3) larger quantity of dye required to obtain the required depth of shade, resulting in lower wet-fastness, lower resistance to dry-cleaning and lower sublimation-fastness;
(4) increased release of oligomers;
(5) reduction in abrasion resistance due to soft, exposed microfibres.

The dyeing of microfibres is described fully in Chapter 7.

2.4.6 Alkaline dyeing

Mitsubishi Kasei, now DyStar Japan, announced a new alkaline dyeing system to the commercial world in 1993 [27]. Most polyester and polyester-blend wet processes are alkaline. The exceptions are dyeing and finishing formulations. Many of the dyes used are based on azo chemistry, as these dyes exhibit high tinctorial strength, excellent build-up and superior fastness. Azo dyes, however, tend to decompose in alkaline baths, especially at the high temperatures used in polyester dyeing. The pH is normally adjusted down to 4–4.5 to protect the weak dyes.

DyStar Japan conducted considerable research to find dyes which would be stable under alkaline conditions [28]. The work led to a complete line of Dianix and Resolin disperse dyes [11], which are stable at pH 9.5–9.9, when used with special buffering agents JpH 95 and JpH 99. The benefits gained by the new procedure include:

(1) over 30% trimer reduction;
(2) cleaner machinery;
(3) time savings (190-minute cycle compared to 270 minutes);
(4) reduced BOD/COD in effluent;
(5) water and energy savings (approximately two-thirds of the cost of the normal dyeing).

2.4.7 Reduction clearing

After completion of the dyeing cycle, optimum fastness is achieved only after clearing away surface deposits of dye which have not penetrated into the polymer matrix. The dyes lying on the surface – especially when dark shades such as cardinal red, navy blue or black have been dyed – will easily rub off or transfer to adjacent fibres after being sewn into garments. An example of a typical reduction clear is:

(1) 5 ml l^{-1} caustic soda 38° Bé;
(2) 2–3 gl^{-1} sodium dithionite;
(3) circulate at 80 °C for 15 minutes.

In order to save time, energy and water, the clearing can take place using the exhausted dyebath after cooling to 80 °C and adding the required chemicals.

If the vessel is a partially-flooded jet, additional hydrosulphite should be added to compensate for the strong oxidation due to the free air space. Goods must be rinsed hot and cold. Acidify with 1–2 ml l^{-1} acetic acid 60% in the final rinse bath.

2.5 CONTINUOUS DYEING OF 100% POLYESTER

The Thermosol process for the dyeing of polyester/cellulose blends is well established. Attempts to transfer this process to 100% polyester fabrics has met with little success except for the dyeing of automotive and aircraft seat belt material and narrow ribbons. The dyeing of interlinings for suiting material and upholstery fabrics has been tried, but not successfully [29]. The process for seat belts, which does not require the critical shade matching of apparel where butting of seams makes evenness critical, has been commercialised. The automotive companies have very strict requirements regarding shade and fastness.

In a typical installation a continuous range is purchased from one of the major narrow-fabric equipment suppliers – for example, Benz, Werner-Mathis, Mageba or Breitbach – and modified by the dyer. The principle is similar to that for polyester/cellulose. Pad dye the mixture, containing the disperse dye, penetrant and anti-migrant, in a two- or three-roll padder with 20–25% pick-up in a small trough to prevent tailing of the bath. Pre-dry and dry on steam-heated cans and Thermosol on thermal fluid-heated cans at 220–230 °C, with high tension to achieve the optimum dimensional stability. The end-use requires as little stretch as possible in actual use. After Thermosoling, 5–6 wash boxes are used for the traditional washing and reduction clear to maximise rub-fastness. The biggest quality problem is lack of penetration into the densely woven substrate. The machine is typically threaded with 4–6 belts running side by side and runs at 30–40 yards per minute. It is common to reserve one range for the very dark black and navy shades and the other ranges for light tans and greys typical of automotive needs.

The dyes selected [30] are the high energy dyes such as the Dianix AM range from DyStar. These dyes and others from other suppliers, give the high sublimation-fastness and high light-fastness (150–200 hours) required in the automotive trade.

2.6 SOLVENT AND SOLVENT-ASSISTED DYEING

Although water is recognised as a universal solvent, interest in the use of non-aqueous solvents, particularly organic solvents, can be traced to the earliest period of the development of cellulose acetate [26; p144]. These solvents were used both as dyeing assistants in water baths and as the dyebath itself. Much of the early work in this area tended to concentrate on less toxic, water-miscible solvents such as alcohols, aldehydes and ketones [31].

Broadhurst reported an early process by Martin for the dyeing of polyester films and fabrics which followed this trend and used solutions to disperse dyes (as press cake material) in water-miscible liquids of high boiling point (such as ethylene glycol or diethylene glycol) [32]. The

goods were immersed for 10–30 seconds at 180 °C, and subsequently washed in water. Medium depths of shade were reported. Also, since the bath was not exhausted, the economical use depended on repeat dyeings of the same hue.

Chlorinated hydrocarbon solvents such as perchloroethylene were strongly considered in the late 1960s and early 1970s, as reported by Broadhurst in a number of citations. Many factors stimulated this work, including the cost of and demand for water. It was felt that these easily recoverable and easily volatilised solvents would solve effluent disposal problems.

As a dyeing medium, perchloroethylene has advantages and disadvantages. It dissolves many disperse dyes, wets textile fibres rapidly and has 'carrier-action' on polyester by reducing the T_g. After dyeing, the low specific heat and low latent heat of vaporisation were strongly noted as an incentive for extensive work to commercialise this process.

The dry-cleaning industry continues to use perchloroethylene as a solvent. Unfortunately, perchloroethylene has disposal problems. Because of poor house-keeping habits, small cleaning businesses allowed waste solvent to get into the surrounding earth and contaminate ground water. In Germany and in the USA, work continues to find replacement solvents for perchloroethylene.

The costs of preparing fresh water and the cost to treat dyehouse wastewater continue to increase. In some areas of the world, the competition for potable water drives industry away from certain regions. New concepts must be evaluated which reduce the dependence on water. Tincher reports that researchers at Georgia Tech. and elsewhere have worked on 'solid-on-solid' projects for years [33]. These projects looked at the viability of ink-jet printing and xerographic reproduction to minimise or eliminate water as a vehicle for colour transfer. Tincher also points to the importance of sustainable technologies – those which have no effect on air or water and that recover and re-use fibres, dyes and auxiliary chemicals.

Researchers at CIBA in Switzerland and at Jasper in Germany worked for a number of years to harness the dissolving power of supercritical fluids for textile purposes. Supercritical CO_2 has been used for years to dissolve caffeine from whole coffee beans, for the extraction of hop flavor in the brewing industry, and many other commercial applications. Could this technology be used to apply dyes to textile substrates?

Researchers at the Deutsches Textileforschungzentrum Nord-West e.V., Krefeld, Germany, have built pilot scale equipment and demonstrated the possibility of using supercritical CO_2 (critical temperature 31.3 °C, critical pressure 72.9 bar) for dyeing unmodified poly(ethylene terephthalate) with disperse dyes [34,35]. This work has been described in a review by Bach, Cleve and Schollmeyer [36], which includes 143 references.

The ecological situation is described in Figure 2.4, where the four-stage water-based process is compared with a two-stage CO_2 system. In evaluation of the product, there was no difference in the shade, fibre properties and fastness when compared with the traditional process. Wash-fastness was better. In summary, the claims are:

(1) complete elimination of water pretreatment and of water pollution;
(2) no need for auxiliary agents;
(3) dyeing requires little time, thereby promoting just-in-time delivery;

(4) no after-treatment, if dyed properly;
(5) carbon dioxide is non-toxic, and can be gained from natural sources and easily recovered and recycled in a dyeing process.

However, the requirement to work at such high pressures has delayed the introduction of dyeing from supercritical carbon dioxide. Small changes in pressure can cause variation in depth of shade, and this has held up commercial development.

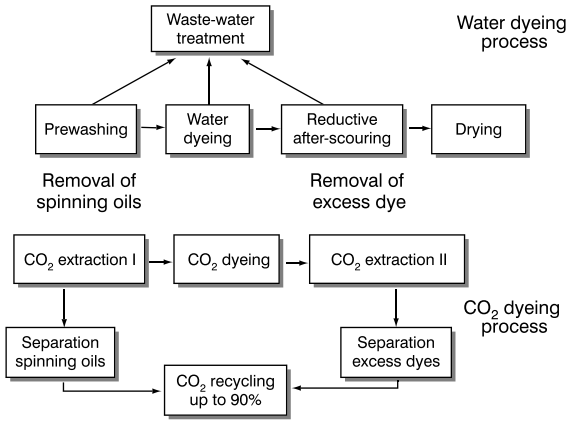


Figure 2.4 Comparison of the dyeing process steps of PET in water and in supercritical CO_2 (from *Rev. Prog. Coloration*, **32** (2002) p89)

2.7 FASTNESS PROPERTIES OF DISPERSE DYES ON POLYESTER

Disperse-dyed polyester materials have, on the whole, remarkably good fastness properties when selected for the correct end-use. Dyes diffuse into the fibre with the use of high temperature in batch and continuous processes and bleed out of the polyester matrix with great difficulty. However, one should not select dyes intended for heat-transfer printing and expect these dyes to perform in the automotive market where extreme demands are made regarding fastness.

When asked about the number of dyes needed in a product line, Kühn said it would depend on whom you asked [37]. A marketing manager would probably want only 20. The technical person, who must solve customer problems in a number of different industries with differing requirements, would say that you should have as many as possible, and with the Colour Index enumerating several thousand available disperse dyes, that presents quite a challenge. In Japan, prior to restructuring in the 1980s and mergers with European companies, it was not unusual for a company to offer 200–300 different products. The number has been reduced considerably in today's market – 140 seems to be an acceptable number – broken into the following categories:

(1) normal HT dyeing;
(2) carrier dyeing;
(3) alkaline dyeing;

(4) continuous dyeing;
(5) printing;
(6) fluorescent dyes;
(7) carpet;
(8) automotive.

The AATCC Buyer's Guide lists between 42 and 117 disperse dye products offered by each of the leading suppliers in the USA [38]. It is recognised that this listing is not complete.

Before selecting dyes, one should consult the supplier's pattern card for a wealth of information. Broadhurst, 25 years after commercial introduction of polyester, was able to write '*very few gaps now remain in the colour ranges that can be selected for any chosen end-use*' [32]. Today, more than 20 years later, new dyes have been introduced, and the available range now serves almost every conceivable need.

In order to achieve the optimum in overall performance, polyester has increasingly been specified for automotive interior furnishings, where exposure to long periods of sunlight at high temperatures and humidity push fastness properties to the limit. Special tests have been developed for this industry.

Although the selection of special dyes is of primary importance, some additional protection can be achieved by the use of UV-absorbers – colourless aromatic compounds that act as 'shock absorbers', preferentially absorbing incident UV and diffusing the energy. These products can be applied during dyeing and protect both fibre and dye. Typical products include benzoates, benzophenones and benzotriazoles [39].

Wash- and sublimation-fastnesses are the most important fastness properties along with light-fastness. Provided the surface of the fibre is properly scoured after dyeing, fastness to washing is generally related to molecular size and the migration of dye. Today, most dyestuff manufacturers also have a range of dyes with high wet-fastness. These have often been introduced with microfibres in mind.

Fastness to heat treatment is required, so that the dyed fibre may withstand conditions encountered later during ironing, pressing and pleating during the assembly of apparel and consumer care of garments. Piece-dyed goods are generally heat-set after dyeing and must retain the dye. Colour-woven and colour-knit fabrics must withstand subsequent high-temperature finishing. Even a slight stain on white or pastel fibres and yarns will be apparent after heat treatment. The greatest faux pas for a garment company is to select poor fastness, deep-dyed panels and sew them side-by-side with white panels. The end result will never be commercially acceptable.

In interpreting the results of laboratory tests for fastness to heat, it should be recognised that the effect of contact heat for a given temperature and time is much more severe than that of hot air in a stenter for the same 'conditions'. Heating-up time is dramatically lower for contact heat. Broadhurst suggests that contact heating tests produce results similar to those obtained by stentering for the same time at a temperature some 20 °C higher [32]. For garment applications, it is essential to know subsequent processing temperatures. Legislation regarding mandatory

temperature and chemical information on care labels has been a great help to the consumer faced with making decisions on how best to care for clothing.

Customer complaints of low fastness to perspiration or water in polyester apparel are always associated with the presence of loose dye particles on the fibre surface. Perspiration and water tests are carried out at 'blood' temperature (37 ± 2 °C), while domestic laundering processes are usually carried out at temperatures in the range of 20–60 °C. Under these conditions, the diffusion of dye from within is very slow and is unlikely to lead to problems, except in very heavy depths of shade and choice of inappropriate dyes. However, the presence on the fibre surface of unfixed dye equivalent to as little as 20 mg kg^{-1} fibre can produce noticeable staining on white threads [32]. The use of after-scouring and reduction-clearing treatments, as noted in earlier sections, will minimise these problems.

Even when the dyer and finisher has released a perfectly 'clean' fibre surface, there remains the possibility of diffusion when the wrong dye is selected for the application and the consumer ignores care label information.

The combined effects of finishing chemicals and heat treatments coupled with the effect of storage conditions can have a negative influence on the fastness of polyester dyeings. This phenomenon is called 'thermomigration'. It is necessary to carefully select compatible chemicals and dyes to minimise this.

2.8 CORRECTION OF FAULTS IN DYED MATERIALS

In spite of the excellent care taken in today's world to meet the requirements of the ISO 9000 standard and guarantee continuous supply of problem-free synthetic fibre, dyestuffs and auxiliaries, the fact is that careless or improper use of even the best chemicals will guarantee less than optimum results. Koksal and coworkers have shown the number of opportunities for failure in a 'fishbone' diagram for the dyer (Figure 2.5) [40]. It is a wonder we are able to produce commercially acceptable dyeings with any degree of regularity.

2.8.1 Migration

Unlevel dyeings can be corrected by treating at high temperatures, preferably slightly higher than the dyeing temperature, with the addition of a levelling carrier. The recommended recipe is:

(1) 1 gl^{-1} dispersing agent;
(2) 1–4% owf levelling carrier.

Adjust pH to 4.5 with acetic acid, raise the bath temperature to 125–135 °C and circulate for 1–2 hours.

The additional time and high temperature allow the penetration of the levelling carrier and release of concentrated dye. Because of the affinity of the dye for the fibre, the segmental motion of the polymer releases dye into the fresh bath and allows re-adsorption and diffusion to regions of lower dye concentration.

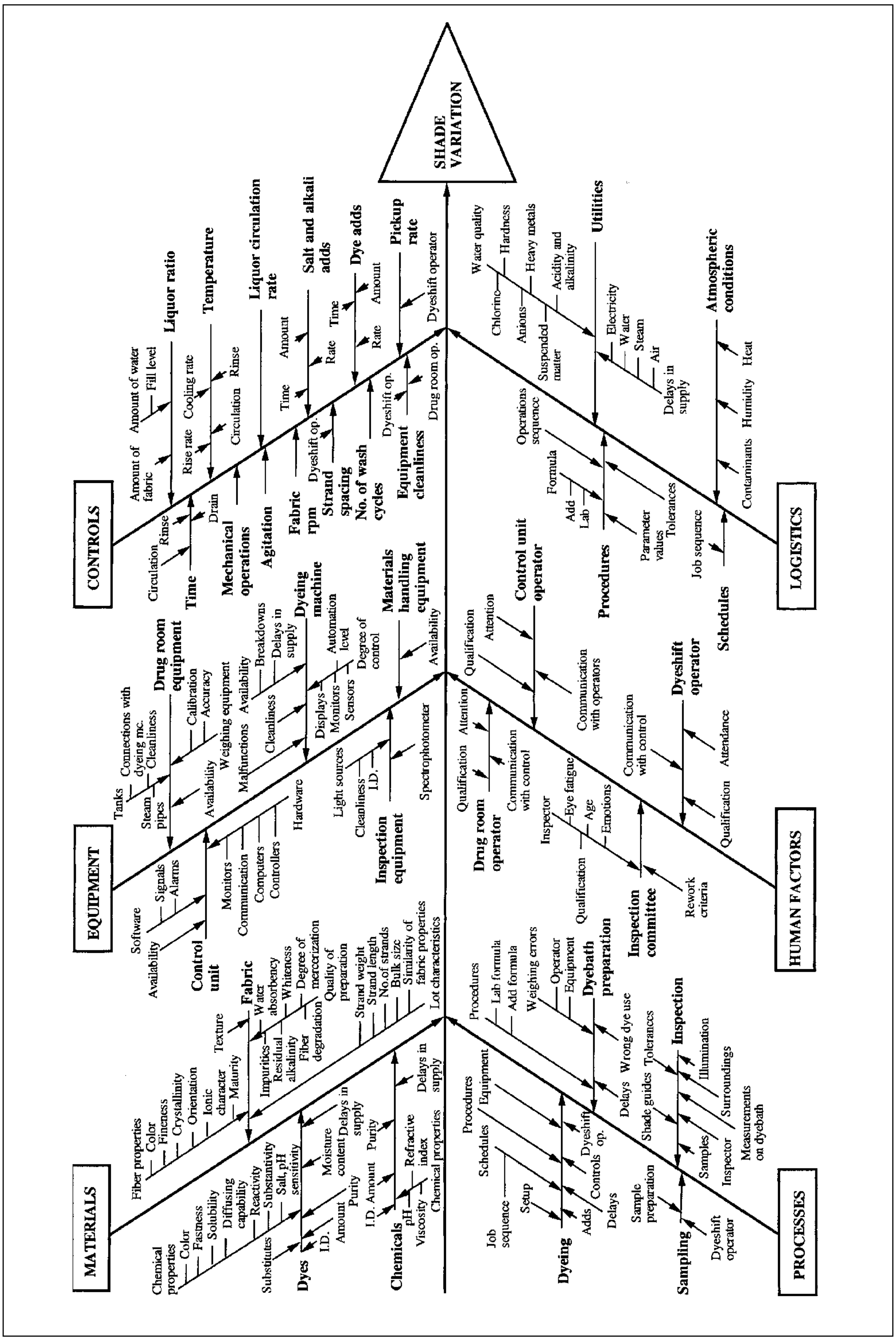


Figure 2.5 Cause and effect (or fishbone) diagram for shade variation in piece dyeing (from [40] p34)

The amount of carrier specified will vary by experience with the construction of the goods, the circulation characteristics of the dyeing machine, and the liquor-to-goods ratio. The higher the temperature, the better the effect, since higher temperature allows freer segmental motion and speeds the diffusion of dye molecules.

2.8.2 Lightening the shade

Occasionally, and especially for first trials on a new shade, the dyeing will come up heavy. A good lightening effect can be achieved by preparing a fresh bath using larger amounts of carrier and levelling auxiliaries. The bath should be taken to at least 130 °C and circulated. Time at temperature will depend on the degree of lightening required, the liquor ratio and the machine characteristics.

2.8.3 Stripping

The shade card supplied by the manufacturer should be consulted to determine whether a reductive or oxidative treatment is recommended. The optimum stripping can typically be achieved by using both methods, one after the other, but damage to the handle of the goods, and time factors, usually preclude using two separate procedures. Preliminary tests in the laboratory are usually advisable in order to maximise the effectiveness of the treatment and minimise the damage to the goods.

Reductive Strip – the first choice:

(1) 2–4 ml l^{-1} caustic soda 38 Bé;
(2) 5 gl^{-1} sodium dithionite;
(3) 4% owf reduction-resistant carrier;
(4) circulate the bath, for 30 minutes at 120 °C.

Oxidative Strip – not usually recommended:

(1) 3 gl^{-1} sodium chlorite;
(2) 4% owf oxidation-resistant carrier;
(3) 2 gl^{-1} sodium nitrate;
(4) adjust pH to 3.5 with formic acid and circulate the bath, for 60 minutes at 125 °C.

In both cases, drain and rinse with fresh water.

2.9 FINISHING PROCESSES

The term 'finishing' covers a wide variety of processes used to modify surface and other properties of polyester fibres, to produce performance characteristics for the next process, or for the intended end-use.

Processing aids are often used and the most important group of such processes concerns the reapplication of fibre-processing aids to tows, staple fibre loose stock, slivers and yarns after

dyeing. The processing aids must have both lubricant and antistatic properties, must be uniformly applied at the correct level, often at high processing speed, and must be applied within narrow tolerance limits [32; p184–92]. Finally, they must be easily and completely removable in fabric finishing.

Re-lubrication of dyed yarn can be achieved either in the dye machine or during the rewinding which follows dyeing. Staple fibre yarns require only a light lubrication for most end-uses, which can be applied as a wax emulsion from a warm final-rinse bath to leave 0.3–0.5% owf after drying. Filament yarn, due to its inherent smoothness, requires less than 0.3% owf and is applied from a kiss-roll during coning (winding).

In order to cut costs and a processing step, yarns dyed on conical packages can often be used directly without rewinding. The lubricant, applied in the dyehouse final rinse, can be a wax or silicone emulsion.

Yarns from a cylindrical dye package normally must be rewound onto paper cones prior to use and may be lubricated more effectively and more evenly than possible from rinse bath application. Self-emulsifying oils should be used for flat and textured filament yarns. Add-on varies from 2.5% to as high as 5% owf depending on the next process [32; p184–92]. Too much add-on can actually add viscous drag and should be avoided.

Mineral oils are often used to lubricate textured yarn. These yarns, when woven into garment labels and left unscoured, have been known to suffer severe bleeding of deep wine red and navy blue shades during storage in hot, humid conditions. Scouring prior to storage is essential. The use of unmodified paraffin wax discs should be avoided, as this wax is difficult to remove.

Annis and coworkers reported research on the control of flame retardant migration [41]. The use of high molecular weight polysaccharides such as xanthan gum in concentrations of up to 2 gl^{-1} in pad baths, enabled the researchers to provide reproducible fixation on 100% polyester drapery material and the use of much lower concentrations of flame retardant to achieve satisfactory flammability results.

2.10 THERMOFIXATION

When PET is dyed with disperse dyes, the rate of dyeing continues to increase as the process temperature is raised. Early commercialisation of polyester as a textile fibre was delayed by the lack of high-temperature processing equipment and the preconceived idea that dyes must be in an aqueous bath in order to penetrate fibres.

Gibson and other researchers at DuPont ran trials in 1947 using only the dry heat of a domestic iron used to press clothing [42,43]. At temperatures in the neighbourhood of 200 °C, they were able to transfer dry colorants from one fabric through an intervening sandwich of undyed cotton onto an undyed polyester fabric. The Thermosol process was born. Commercial acceptance was not immediate despite extensive trials by DuPont. The development of fabrics woven on wider and wider looms which required new wet-processing equipment and the advent of permanent press were the impetus to commercialisation.

The fabric, usually a woven, blended fabric of polyester/cotton or polyester alone, is padded through a trough containing the disperse dye and auxiliary chemicals, dried and baked in the range of 190–225 °C, typically 210 °C, for 30–120 seconds. Substantivity of disperse dyes for the polyester is high under these conditions and the fibres become well penetrated by the dyes within a few seconds of reaching the oven temperature. No chemical accelerant is required. The process times of 30–120 seconds are required mainly to heat the material to the required temperature. If the process continues beyond this time, dye leaves the fabric and the shade is lightened. Anyone familiar with the process is well aware of dye deposits on the side walls of the Thermosol ovens.

The process is mainly used in the dyeing of polyester/cotton blends, particularly woven poplins and twills where it is possible to sell large volumes of a single shade. In order to make the process economical in today's 'just-in-time' market, machinery developments have focused on short-run and quick-change modifications.

It has been shown by numerous researchers that, after removal of the aqueous padding liquor by drying, the majority of the disperse dye is located in and on the hydrophilic cellulosic portion of the blend. The transfer of the dye from there to the polyester is the first phase of the fixation process. *'There is also convincing evidence that this transfer takes place substantially in the vapour phase, rather than by contact migration. Excellent correlation has been shown between 'ABCD' classification of disperse dyes (based on an observed relationship between sublimation-fastness and cover of rate-of-dyeing differences in the fibre) and the proportion of dye that is ultimately fixed on the polyester component of the blend after pad–Thermosol dyeing. Optimum transfer is obtained with dyes of 'B' and 'C' classes. 'D' types showed low transfer because of their low volatility, while 'A' types were so volatile at these temperatures that much of the dye escaped from the system. A residue of disperse dye remains on the cellulosic portion and must be removed if good wet-fastness is to be achieved. If a disperse–vat dye system is used, the disperse stain is removed during the reductive clear and after-soaping phase of the standard procedure. In single stage systems such as disperse–reactive systems, where no reductive clear is possible, the dyer must select disperse dyes with minimum cross-staining or dye the polyester first and depend on the after-wash for reactive dyeing to provide adequate cleaning'* [32].

On 100% polyester fabric, the pad–thermofixation process is used mainly for narrow fabrics, such as ribbons, tapes and automotive seat belts [32]. During the padding, the dye liquor must move into the window pane areas between yarns and, to a lesser extent, between fibres. Transfer follows the same procedure as with blends.

2.10.1 Dyeing procedures

Preparing the pad liquor

Disperse the dyes in approximately 5–12 times their volume of softened water at a temperature of approximately 25 °C. It is essential to strain the dye mix through a fine-mesh greige cloth filter before transfer to the mixing tank. This minimises the possibility of passing poorly dispersed colour to the padded goods. Add an anti-migrating thickener, a dispersing agent and a wetting

or re-wetting agent, all in diluted form. The temperature of the mix and padding liquor should be 20–30 °C. A typical recipe is:

(1) *x* gl^{-1} disperse dye;
(2) 5–10 gl^{-1} anti-migrant;
(3) 0.5–2 gl^{-1} wetting agent;
(4) 0.5–2 gl^{-1} anionic dispersing agent.

Auxiliary chemicals should be used sparingly. A suitable low-foaming wetting or re-wetting agent is needed to ensure rapid and even penetration of the prepared goods. Poor preparation requires additional chemicals and slower processing. A drop of water just placed on the surface of well-prepared goods should lose its specular reflectance in less than 1 second; 1–3 seconds can be acceptable. Anything above that should initiate an investigation and the cause be corrected. Poor dyeings will result from such goods, since contact time in the padder is typically less than 1 second. A polyacrylate-based thickener with high viscosity is required to minimise migration of dye molecules during drying. At higher water content, dye molecules are transported to the point of evaporation. Infrared pre-dryers must be designed and operated to minimise cross-machine drafts. An anionic dispersing agent may be needed if pad liquor stability breaks down during highly turbulent conditions.

Padding

Padding is generally carried out at room temperature in a two-roll padder with 40–70% wet pick-up. Heavier canvas and duck may require a three-roll padder with double dip and nip. The liquor pick-up must be uniform across the face from side-to-centre-to-side, and as low as possible to minimise migration. Adjustable deflection padders have been the industry standard since the 1960s. The opportunity for migration to promote uniformity is not available in continuous dyeing.

Pre-drying/drying

Contact-free drying in the infrared dryer to a residual moisture content of approximately 30% prevents mark-off on the following guide rolls and, particularly in the case of light-weight woven fabrics, gives the fabrics a better appearance. The rolls are normally Teflon coated. Fabric leaving the dryer must be bone dry and immediately enter the Thermosol oven.

Thermosol process

The final fixation of disperse dyes takes place in the temperature range of 200–220 °C in hot air or on contact drums. A wide variety of equipment has been developed for this purpose. The treatment lasts 30–60 seconds for most polyesters under hot air conditions and 15–30 seconds with contact heat.

After-treatment

In order to obtain the optimum fastness and more brilliant shades, an after-treatment is recommended to remove dyes which have not fully penetrated the fibre surface. For woven fabrics of 100% polyester, an alkaline-reductive clear is recommended with:

(1) 8–10 gl^{-1} sodium dithionite concentration;
(2) 8–10 gl^{-1} caustic soda 38 Bé (32.5%);
(3) 0.5–1 gl^{-1} dispersing agent at 70 °C.

The goods are normally treated continuously through an open-width washing machine. With polyester/cellulosic blends, it is usually sufficient to soap at the boil in the open-width with 1–2 gl^{-1} non-ionic scouring agent in order to remove excess dye from the surface.

2.11 DISPERSE DYES FOR THE AUTOMOTIVE INDUSTRY

The automotive industry is a very large, specialised market which demands special attention. Polyester is certainly not the only fibre used in the industry. It is, however, the major fibre in a number of categories (Table 2.5).

Table 2.5 Percentages of markets for polyester in the automotive industry

	(%)
Seatbelts	100
Headliner and door covering	77
Seat upholstery	66
Carpet for the floor and trunk	23

In total, polyester claims approximately 59% of the total fibre content used in the automobile [51]. In 1993, 47.5 million cars and trucks were produced world-wide. The market for dyes was between 2000 and 2100 metric tonnes with the majority going to Japan (600 tonnes), the USA (550 tonnes) and Europe (500 tonnes). The total fibre content of these automotive products, including cars and trucks, was 210 000 tonnes of which 59% was polyester (124 000 tonnes). If the average shade was 1.5%, the consumption of disperse dyes amounted to 1860 tonnes.

The Japanese dye market is supplied by four major domestic suppliers – DyStar Japan, Sumitomo, Mitsui and Nippon Kayaku; the European market is supplied by Ciba, Dohmen, DyStar, Clariant and BASF; the USA market is supplied by all of the above. A desire to have uniform requirements in all plants, and to manufacture components in one country and ship to other countries, has resulted in a dyestuff selection which meets the many market requirements. The market share and particular distribution of dyes varies from market to market to suit local tastes and to meet the fastness requirements for that market (Table 2.6). White cars are very popular in hot climates such as Florida – white reflects the sun light and keeps cars cooler; black is

Table 2.6 Automotive market share by colour

Dye colour	(%)
Yellow/orange	35–30
Red	25–15
Blue	30–35
Other	10–20
Total:	100

not as popular because of the tremendous heat absorptive capability of black. Certain green shades, which were very popular in Europe, would not have sold in the USA, and so on.

2.11.1 Fastness requirements

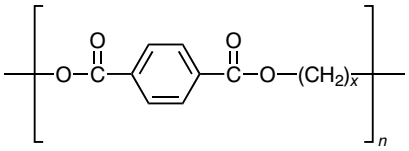
The automotive industry has very strict light-fastness requirements. Autos today have a much greater life expectancy than in the past. Thirty years ago in the USA, the average car owner was expected to trade his car every three years; today, cars are kept for 6–7 years before being traded or returned by the first owner. Leased cars are typically kept for three years. Ultraviolet is the major contributor to fading.

UV absorbers of the benzotriazol type absorb UV in the 270–350 nm range, whereas the benzophenone type absorb in the 350–700 nm range. Together they cover the range required by the coalition of German automotive manufacturers, FachKReisAutomobile (FAKRA), and the Society of Automotive Engineers (SAE) for automotive applications. The triazine derivative is a second generation UV absorber that is high energy, sublimation-fast, which is important for the demands of the automotive market.

2.12 NEW POLYESTER FIBRES

2.12.1 PTT and PBT

So far, this chapter has dealt solely with fibres manufactured from poly(ethylene terephthalate) (PET), but several other polyester fibres have recently become available, some for specialised markets. Most of these use alternative diols to 1,2-ethane diol (ethylene glycol). Two important variants are poly(trimethyl terephthalate) (PTT) and poly(butylene terephthalate) (PBT), also known as 3GT and 4GT. The structures of PET, PTT and PBT are shown

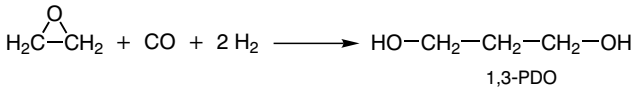


2.18

where $x = 2, 3$ or 4
n = DP

below (**2.18**), where $x = 2$, 3 and 4, respectively. Of these, poly(trimethylene terephthalate) (PTT) is probably the most significant [44]. A more appropriate name might be poly(propylene terephthalate) (PPT) in view of the names adopted for the other two polymers. The Shell Chemical Co. introduced the fibre, named Corterra, in 1995.

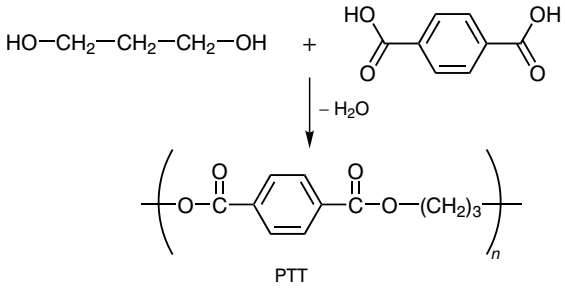
The reason PTT is beginning to be produced on a large scale is the discovery of an economical route to the synthesis of the monomer 1,3-propane diol (1,3-PDO), as shown in Scheme 2.1.



Scheme 2.1

The polymer is prepared by melt condensation of the diol with terephthalic acid (Scheme 2.2). It competes with nylon in carpets [45] and with PET and PBT in textiles [44]. Some of the important properties of PTT in comparison with those of other polymers are shown in Table 2.7 [44].

Lower temperatures are recommended for pre-setting, dyeing and heat setting PTT compared to PET, and a major bonus is the fact that it can be dyed at 100 °C without the use of carriers. This applies particularly when low-energy type disperse dyes are employed [46]. A typical dyeing cycle is shown in Figure 2.6.



Scheme 2.2

Table 2.7 Properties of thermoplastics used in fibre production [44]

	Property				
Polymer	Melting point (°C)	Glass transition (°C)	Density (g cm^{-3})	Water absorption[a] (%)	Water absorption[b] (%)
PTT	228	45–65	1.33	0.03	0.15
PET	265	80	1.40	0.09	0.49
Nylon 6	220	40–87	1.13	1.90	9.50
Nylon 6.6	265	50–90	1.14	2.80	8.90

a After 24 h
b After 14 days

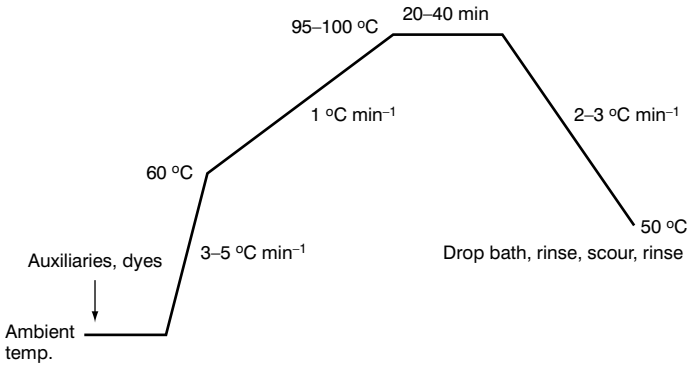


Figure 2.6 Dyeing cycle for PTT with low-energy dyes

Recently, DuPont Textiles and Interiors have introduced a stretch bicomponent polyester fibre – Lycra T400 [47]. The basis of this technology is a spinning technique in which two different polyester polymers are spun simultaneously, side by side. In this case, the dissimilar properties of PET (2GT) and PTT (3GT) are used to impart new stretch properties naturally induced in the fibre, and not developed during a texturing process. The much higher shrinkage of the PTT gives the fibre a novel crimp effect. This is further developed by heat and processing – for example, during scouring or in the dyebath.

Fabrics incorporating the bicomponent yarn demonstrate good easy-care properties with low shrinkage and excellent wrinkle resistance, and garments are claimed to show outstanding crease sharpness and crease retention. An important advantage over polyurethane elastomeric fibres is that T400 has good resistance to chlorine bleach.

Recommended processing routes are to heat set prior to dyeing at between 160 and 170 °C, dye with medium to high energy (for disperse dyes at 125–130 °C or post-set), being careful not to exceed 160 °C. Reduction clearing after dyeing is recommended, but due to the lower T_g of PTT, this should be at carried out at 70 °C.

2.12.2 Poly(lactic acid)

Poly(lactic acid) (PLA) has been described in Chapter 1 (Section 1.6.4). There is increasing interest in fibres spun from it because it is claimed to be biodegradable (but see comments in Section 1.6.4). The fibres and fabrics are dyed with selected disperse dyes [48]. There is often a difference in shade when compared with that obtained when PET is dyed with the same dye [49]. However, it is not unusual for the substrate to produce differences in shade when dyeing with disperse dyes.

More serious is the deleterious effect on physical properties of dyeing PLA at high temperatures [50]. Severe loss of tensile strength in PLA yarns occurs on dyeing at 130 °C, accompanied by a loss in elongation, due to substantial hydrolysis. The maximum recommended dyeing temperature for PLA is therefore 110 °C. Yang and Huda [50] recommend the

dyeing cycle shown in Figure 2.7. Very little dye is taken up below 80 °C, so the rate of increase in temperature of the dyebath (ramp) can be steep up to that point. However, once dye sorption commences, the rate of increase should be much lower (1–2 °C min^{-1}). It may even be necessary to hold the temperature at 90–95 °C for 5 minutes for good levelness to be obtained. The recommendation for the time at the maximum temperature of 110 °C is 30 minutes. Cooling at 2 °C min^{-1} to 50 °C should be sufficient to avoid fabric creases, since the T_g of PLA is thought to be about 58 °C.

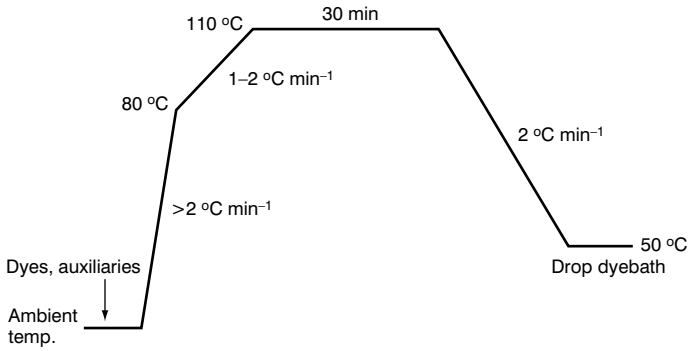


Figure 2.7 Recommended dyeing cycle for PLA

Other significant findings concerning the dyeing properties of PLA fibres were that although the rate of diffusion of disperse dyes into fibres is much higher for PLA than it is for PET, the equilibrium saturation concentration is generally much lower [49]. This leads to poor build-up for anything other than pale shades. Despite this, the colour yield on PLA fibres is quite good, since the refractive index of PLA is much lower than that of PET (1.40 and 1.58 respectively).

PLA also has a much higher transmittance for UV radiation than PET. This in turn leads to inferior light-fastness properties of disperse dyes in PLA, especially blue dyes. It may therefore be necessary to select dyes carefully and consider the use of UV absorbers.