

# The selection, classification and application of dyes

## Nature of the textile coloration process

The value of most of the textile fibres destined for the domestic market is increased by coloration before they are sold. Unlike the impregnation of paper with coloured ink, the processes by which a molecule of dye becomes attached to a textile fibre involve far more than a simple impregnation process. Uniform impregnation of the fibre mass is only the preliminary requirement. It is the chemical interaction between a dye and a fibrous polymer, as well as the movement of dye into the fibre structure, which determines the suitability of the final product for the purpose in hand.

Most textile dyes are applied from water or a water-based printing paste. Many dyes for textiles are soluble in water and, like simpler electrolytes, their molecules split into positively and negatively charged ions. With most dyes (*acid dyes*) the coloured ion is negatively charged, i.e. it is an anion. Some dyes, however, form positively charged coloured ions, i.e. cations. Commercially these are limited in number but they meet specific needs, particularly with acrylic fibres. As a class they are referred to as *basic dyes*.

## Interaction between dye and fibre

A dye is taken up by a fibre as a result of the chemical attraction between them, but as explained in Chapter 3 the dyebath conditions need to be adjusted before the attractive forces can operate efficiently. When fibres are immersed in water they develop a negative charge. Since the sign of this charge is the same as that on the dye anion, the fibre repels the dye, hindering or even preventing its close approach. With most water-soluble anionic dyes the addition of an electrolyte, such as common salt, enhances the attraction by masking the negative surface charges of the fibre, and the dye uptake is therefore increased.



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Chemical combination through the formation of a covalent bond is the strongest possible dye–fibre attachment (Table 3.2, page 38). Next in strength are the salt links, which are less than one-quarter as strong as a covalent bond. Whilst covalent bonds can only be broken by a chemical reaction, other dye–fibre links can be split by the action of heat and water. It is therefore possible to control the rate of dye adsorption and ensure a uniform distribution of dye by raising the temperature of the dyebath. For this reason many dyeing processes are carried out at the boil.

Dyeing conditions are chosen to ensure that the final distribution of dye between the dyebath and the fibre always favours the fibre. But, like many other chemical reactions, the take-up of dye is reversible, and if the dyed fabric is placed in clean water the dye may bleed out in an attempt to re-establish equilibrium. Here therefore is a potential cause of poor wash fastness.

### **Affinity and substantivity**

Information concerning the strength of the binding forces between dye and fibre is obviously valuable for dye selection, since it is relevant both to the colour yield obtained from the dyebath and to the fastness to wet treatments of the end result. The combined strength of the molecular interactions involved is referred to as the *affinity* of the dye for the substrate. This is a thermodynamic quantity that can be measured, so dye selection can be aided by ranking the members of any one class of dye in order of affinity.

Reliance on such measurements is restricting, however, because affinities are measured under precisely defined conditions of temperature, pH and salt concentration. The values obtained offer a comparison between dyes only under the conditions specified, and they do not apply to any other dyebath conditions. Conditions always change during a dyeing process, and the less specific term *substantivity* is more useful to the practical dyer because it can indicate the level of exhaustion (that is, the extent to which the dye has disappeared from the dye liquor into the goods). This in turn has a bearing on the wet fastness of the dye–fibre combination. Generally the affinity of a dye for a particular substrate does bear some relationship to the substantivity under practical application conditions, and the two terms are often, though strictly speaking incorrectly, used interchangeably.



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### **Fundamental behaviour of dyes**

In the dye–fibre reaction one reactant, the fibre, is a solid and the other, the dye, is dissolved in water. With any reaction, molecules (or ions) must collide before they can react together. In a solution, the

molecules are in a state of constant random motion. But inside fibres the polymer structure offers marked resistance to the movement of the dye molecules, so that prolonged dyeing times are often needed before interaction is complete. Dyeing conditions therefore are always chosen so that they assist the movement of dye into the fibre, so enabling the forward reaction to go as efficiently as possible. The specific reactions concerned depend on the chemical character of the fibre, and therefore choice of dye is restricted to those capable of interacting in the appropriate manner.

Some colorants become retained within the fibre as a result of the mechanical entrapment of water-insoluble pigments, a mechanism which along with the formation of a covalent bond gives the highest level of fastness to wet treatments. Even so, the initial stages of application still depend on attractive forces between fibre and dye. In this case the colorant is initially applied in water-soluble form, and appropriate reactions in the fibre are then brought about. The colorant is chemically converted into the insoluble form at the end of the exhaustion step.

Once the appropriate dye class for the fibre in question has been chosen, attention has to be turned to the substantivity of the dyes required to provide the necessary level of fastness properties. This also involves choice of the method of application best suited to the dye combination. It is at this stage that the classification of dyes by appropriate dyeing procedures becomes especially relevant, and these matters will now be considered in more detail.

### **Selection of dyes for wool**

In the coloration of wool the consumer generally benefits more from the requirements of the manufacturing processes than the demands made by the end use of the fabric. Both before and after dyeing, wool undergoes various wet treatments that concern the dyer even though they are not his responsibility. Efficient preparatory treatments of the material are the key to good dyeings, whilst the success of subsequent wet treatments is generally reliant on the proper selection and application of suitable dyes. Since the conditions of post-dyeing processes are usually more severe than those of any normal aftercare treatments, dyeings that have proved satisfactory during the processing will possess more than adequate fastness properties for consumer use.

Technical requirements also depend on whether the fibre needs to be dyed as loose fibre ('loose stock'), combed wool in the form of an untwisted strand of parallel fibres from the combing operation ('top'), yarn or fabric. With each type of substrate particular criteria have to be met in



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order to produce the required quality of colour, and this is usually achieved through variations in the dyeing conditions.

### ***Loose fibre***

When dealing with loose fibre, slight variations in depth of shade (*unlevelness*) from batch to batch may be dealt with by blending fibres from different batches. A uniformly coloured product is thus obtained before it is converted into yarn and woven into fabric.

There is less tolerance of batch-to-batch variations for some uses than others. For example, batch-to-batch variations need to be kept to a minimum with combed worsted fibres intended for high-twist yarns to be used in suitings and gabardines. On the other hand, in yarns for fabrics such as Harris tweeds different coloured fibres may be blended together to produce a multicolour effect (Plate 4). Clearly small variations in levelness from one fibre batch to another are not critical in this case, but since fabrics so produced are often destined for suitings, fastness to light and wet treatments become more important.

### ***Yarn***

The choice of dyes and dyeing conditions for the coloration of yarn is much more critical than for loose fibre because level dyeing and accurate shade control are of paramount importance. The fastness requirements will depend on the destination of the yarn. For example, hand-knitted or machine-knitted goods are never subjected to the severe processing encountered in woven fabrics, and some relaxation in wet fastness standards will therefore not detract from the expected quality of the knitted goods. Such yarns are usually dyed as hanks to preserve their characteristic softness and bulkiness, but yarns for weaving or for industrial knitting machines are dyed on wound packages (see page 114), which require more attention to dye distribution, liquor circulation and levelling.

Machine-washable wool demands careful attention to choice of dye class because the shrink-resist finishes often have the effect of reducing the wet fastness of deep shades; reactive dyes usually give satisfactory results, however (see page 86).

### ***Woven fabric***

Woven fabric requires both very level dyeing and excellent fastness properties, the latter being necessary to withstand the remainder of the finishing processes. These range from the removal of



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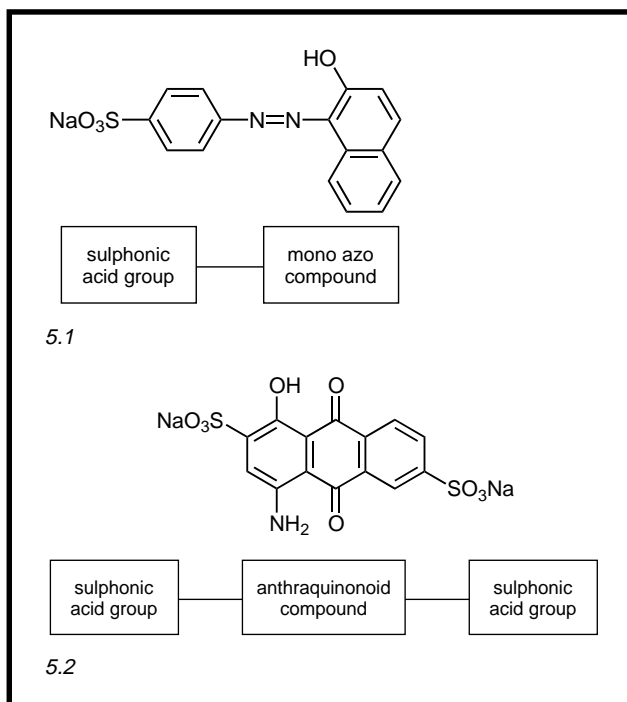


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spinning oils by a scouring treatment of a few minutes duration in a weakly alkaline detergent solution to more severe treatments in steam (*decatising*), boiling water (*crabbing* and *potting*), chemical treatments (*setting*) and mechanical treatments of wet fabric (*milling*), all of which impart particular characteristics required for the end use of the wool fabric. It may be necessary also to treat the dyed fabric with 5% sulphuric acid solution, followed by drying and baking (*carbonising*), to facilitate the removal of burrs. None of these treatments will be encountered by the fabric after it leaves the factory and they are all more severe than conditions encountered in normal aftercare.

## Acid dyes

The first synthetic dyes for wool were the acid dyes (see page 76), a class of dye that has since grown into a large, diverse, versatile and widely used group.



Acid dyes are sufficiently soluble to allow direct application from an aqueous solution. Some acid dyes may also be used for the coloration of other animal fibres, including silk, and also of nylon, which like protein fibres has both amide linkages and amino groups in its structure (page 59).

### Nature of acid dye molecules

Acid dye molecules provide a wide range of colours covering several different chromophoric systems, based on anthraquinone, azo, triarylmethane and azine structures, and can also be applied under a wide variety of conditions.

All acid dye molecules have certain features in common. They all possess at least one group of atoms that imparts solubility in water to the large coloured component of the molecule. This is usually, but not always, the sodium salt of a sulphonic acid group,  $-\text{SO}_3\text{Na}$  (5.1 and 5.2 are typical acid dyes, and further examples are given in Appendix 1).

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The sulphonic acid group (or in some cases the carboxylic acid group) is also important in linking the dye to the fibre, since it can react with a basic group in the wool molecule and form a salt linkage, which thus becomes a point of strong attachment. For one group of acid dyes this is the most important reaction to be controlled during application. Sodium salts of sulphonic acids in general behave as simple electrolytes and dissociate into ions but, as explained above, the dye–fibre reaction is only achieved after the large coloured anion has diffused into the fibre.

Other factors in the attraction between fibre and dye include hydrogen bonds and van der Waals forces. The contribution of the latter is always present, and depends directly on the size of the dye molecule. Whichever type of bond predominates in the final stages of dyeing, the balance between one type of force and another can vary as the process goes on, and this fact is important in the formulation of dyeing methods.

### *Coloration of wool with acid dyes*

Once the shade and the appropriate fastness properties have been selected, the dyer's attention turns to the production of level dyeings. Those dyes that attach to the fibre mainly through salt links are the easiest to dye level, but as the contribution from nonionic forces increases, so do the practical difficulties. In essence, dyeing methods adopted enable control of the rate at which dye–fibre interactions occur.

The easiest acid dyes to control are referred to as *levelling acid dyes*. Without the presence of a strong acid such as sulphuric acid in the dyebath, the important salt linkages between the wool fibre and the dye cannot form. The term 'acid dye' therefore refers to the necessary acidity of the dyebath rather than the chemical character of the dye. These dyes usually remain unaggregated.

Acid dyes are chosen whenever level dyeing is crucial to the quality of the goods. Yarn intended for weaving is one example, since unlevel yarn, when woven or knitted into a fabric, will give rise to localised areas differing in colour from the rest of the fabric. Both levelling and yarn penetration is especially important in carpet yarns, where the fibres of the pile are viewed end-on. Unfortunately their good migration, which makes levelling acid dyes suitable for the production of level dyeings, also means they may easily be removed from wet fabric. They cannot therefore be expected to show a particularly high degree of fastness to wet treatments. Since this factor is fully considered during the dye selection process, it does not usually offer a serious threat to the quality of the end product.



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Once the group of dyes has been selected for level-dyeing properties, satisfactory fastness to light of the dyeing still has to be ensured. Articles like carpets will require dyes of high fastness to light, since they will be expected to keep their attractive appearance for many years. If they are intended for use on ships, then good fastness to salt water will be required as well. Garments also require a reasonable level of fastness to both light and perspiration, but since many are unlikely to need daily cleaning and dry cleaning may be used for aftercare, the fastness to washing need not always be of the highest order. With hosiery, on the other hand, fastness to light weighs less heavily than fastness to washing, and here rather more attention is paid to a group of acid dyes with dyeing properties different from those of the easy-levelling dyes, but which have better fastness to wet treatments.

### ***Application of acid dyes***

The connection between the levelling properties of the dyes and their subsequent fastness to wet treatments allows acid dyes to be classified into groups according to the application procedures that allow the best control of their levelling. The three groups are as follows.

- (a) *Equalising acid dyes*, which level well but have poor fastness to wet treatments. Sulphuric acid is incorporated into the dyebath.
- (b) *Milling acid dyes (acid-dyeing)*, which have poorer levelling properties than (a) but better fastness to wet treatments. They are applied using a weaker acid such as methanoic (formic) or ethanoic (acetic) acid, the acid chosen depending upon the substantivity of the dye.
- (c) *Milling acid dyes (neutral-dyeing)*; these are sometimes referred to as *supermilling* acid dyes. Their levelling properties are poor, but their fastness to wet treatments is excellent.

These groupings represent a transition in dyeing properties rather than clear-cut divisions. Nevertheless, the classification is useful to the dyer in dealing with a class of dye containing members ranging from easy-levelling dyes with poor wet fastness to dyes with very poor levelling properties but high wet fastness.

### ***Equalising acid dyes***

Their ease of fibre penetration, application and levelling, together with their bright shades, make equalising acid dyes (levelling acid dyes) the preferred choice for the coloration of wool, provided fastness requirements can be met.



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For levelling acid dyes the dyebath is prepared with sufficient sulphuric acid or methanoic (formic) acid to give a pH of 2.5–3.5, which promotes exhaustion, and sodium sulphate (Glauber's salt), which aids levelling by providing sulphate ions to compete for the dye sites. The goods are entered into the bath and the temperature raised to the boil over a period of 15–30 minutes. During this time water and sulphuric acid penetrate the mass, and the dye begins to diffuse into the fibre. During the following 45 minutes at the boil, the dye continues to migrate from regions of high to regions of lower concentration until its distribution in the wool is uniform.

### *Milling acid dyes*

More highly substantive dyes are required to produce a better degree of fastness. Adequate levelling through the controlled formation of ionic links using a strongly acidic dyebath is no longer possible, because the overall attractive forces are too strong. For these dyes the dominance of ionic forces then needs to be suppressed by reducing the acidity to a pH of 4.5–5.5 (by using ethanoic acid instead of sulphuric acid), and aggregation is controlled by raising the temperature.

Milling acid dyes give bright shades but their fastness properties are better than those of the equalising acid dyes. Their levelling properties are adequate for fabrics intended for uses such as dresswear, pale- to medium-depth knitting yarns and some types of upholstery. They offer some economy in production compared with the easy-levelling dyes because the similarity of the dyeing properties of the members of the class allows the dyer to reduce the number of dyes held in stock. If one red, one yellow and one blue dye (the primary colours) are chosen, a wide range of shades is possible by mixing the three dyes in appropriate proportions. This makes it easier to replace time-consuming laboratory shade-matching trials by instrumental colour measurements and computerised shade matching.

Another subdivision of milling acid dyes includes acid dyes at the higher end of the substantivity scale. Such dyes require more weakly acidic conditions still. Dyes in this subgroup tend to be more individual in character. Their poorer migration and higher wet fastness usually persuade the dyer to select a dye as near to the required shade as possible to minimise the necessity of shading to the correct colour with additional dyes.

The subgroup as a whole has good fastness to light and is often used to provide heavier shades for womenswear and loose-stock dyeing for carpet yarn and knitwear.



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## *Milling acid dyes (neutral dyeing)*

The highest standards of wet fastness are usually obtained using these milling acid dyes, a group that includes dyes able to withstand the very severe wet-milling processes associated with the preparation of wool fabric. Dyeing is carried out in loose wool and slubbing form because it is too difficult to obtain good levelling on fabric. Very careful control of the dyebath pH between 5.5 and 6.5 is required, and the temperature of the dyebath is raised very slowly in order to achieve level dyeing. These dyes remain aggregated throughout. 'Assistants' such as ammonium ethanoate or ammonium sulphate are used to help in control: these compounds decompose at the boil with the

gradual release of acid, which reduces the pH of the dyebath and completes the exhaustion process.

The acid dye class therefore contains members that can meet a wide range of fastness and level-dyeing requirements, all of which are produced through very careful manipulation of dyebath conditions (Table 5.1).

**Table 5.1** Conditions for dyeing with acid dyes

Acid dye type	Additive	Dyebath pH
Equalising	Sulphuric acid or methanoic acid	2.5–3.5
Milling	Methanoic acid or ethanoic acid	4.5–5.5
Neutral-dyeing	Ammonium sulphate or ammonium ethanoate	5.5–6.5

## **Other dyeing methods for wool**

In general, menswear made from wool fabric will require good all-round fastness properties. For this purpose duller shades are usually more fashionable than those obtained by using levelling acid dyes but, as we have seen, the latter are unlikely to provide satisfactory wet fastness. The best fastness is obtainable with milling acid dyes, but they have poor levelling properties.

Craft dyers deal with this difficulty by using mordants for wool and silk, which enable the colourings extracted from natural products to display a reasonable substantivity. This is reminiscent of ancient and long-abandoned dyeing practices which, by comparison with the present-day synthetic colours, yield fabric with unacceptably poor fastness properties. Nevertheless, the principle can be used to advantage with synthetic mordant dyes in conjunction with more effective mordants.

The principle of mordanting is to form a bridging link between the fibre and dye; the mordants used today are metal ions. Since the most common metal used is chromium, those dyes applied in this way are called *chrome dyes*.

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### *Chrome dyes for wool*

There are several ways by which chromium may become implanted into the dyed fibre. But whichever method is adopted the dye molecule must contain suitably disposed chemical groups, otherwise the dye and chromium ions cannot combine. The reaction is called *chelation*, and some of the more substantive levelling acid dyes may be used in this way. It is therefore possible to have the advantages of level-dyeing acid dyes during exhaustion stage of the dyeing process, and then significantly to improve the fastness properties through aftertreatment of the dyeing with a solution of a chromium salt such as potassium dichromate. Conversion of the dye to a chromium complex substantially increases the molecular size, which prevents the outward diffusion of dye molecules even during severe wet treatments such as potting. The method is known as the *afterchrome* process.

In practice the advantages are accompanied by the pollution of dyehouse effluent by chromium residues, and also by difficulties in controlling and reproducing the final shade, which varies according to the chroming conditions. The afterchrome process is therefore generally used for loose wool or tops rather than for yarn or fabric, so that variations in shade can be eliminated by blending different batches before spinning. Moreover, because afterchroming is a two-stage process, extra time costs are incurred. Fibres also tend to be easily damaged, as the immersion of the wool in the acidic liquor is prolonged. Excess chromium adsorbed on the fibre may give rise to a harsh handle, which is detrimental to the spinning properties. Nevertheless, chrome dyeing is still preferred for some purposes because of the process can yield a product with excellent fastness properties more cheaply than most of the alternatives. It is favoured for the production of very deep shades on loose stock, and blacks and navies on yarn and fabric.

The alternatives to afterchrome dyeing are the so-called *Metachrome process*, in which dye and mordant are applied simultaneously, and *chrome mordanting*, in which the chromium is applied before dyeing. These offer no advantage over the afterchrome process, however, and their use is not widespread.

In the final analysis their economy of application, high fastness and level dyeing make chrome dyes among the most extensively used wool dyes.

### *Metal-complex dyes*

Further developments aimed at avoiding the problems arising with chrome dyes have led to



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combination of the chromium with the dye molecules by the dye manufacturer. This eliminates variations in shade due to uneven afterchroming, and maintains the good fastness to both light and wet treatments of afterchrome dyeings. Such dyes are called *metal-complex dyes*, and their properties depend in part on the number of dye molecules attached to each chromium atom. The earliest complexes incorporated one chromium atom into each dye molecule (1:1 complexes) and could be applied as levelling acid dyes provided the dyebath was made strongly acidic. They combine the easy-levelling properties of the levelling acid dyes with improved light and wet fastness. Unfortunately the stronger acidic conditions inevitably lead to fibre damage and associated difficulties in spinning. Nevertheless, where the needs for good penetration, levelling and light fastness are paramount – as with gabardines and some high-twist carpet yarns – some fibre strength may be sacrificed. Moreover, dyeing acid-milled fabric or carbonised fabric in this way eliminates the need to neutralise the acidified wool before dyeing.

The necessity of a highly acidic dyebath was ultimately counteracted by further development of chrome–dye complexes in which each chromium atom is linked to two dye molecules (1:2 complexes). Such dyes may be applied from a weakly acid dyebath to produce higher wet fastness than the 1:1 complexes, and thus can provide good fastness without causing fibre damage. Unfortunately the improvements are also accompanied by a commensurate difficulty in producing level dyeings and consequently 1:2 complexes are not easily used for dyeing fabrics. They are often used along with dyebath additives to prevent the differential coloration of wool fibres from root to tip, a common phenomenon due to the slight changes in chemical composition caused by progressive weathering of the fibre tips during growth. It is referred to as ‘tippy’ dyeing, and 1:2 complexes often exaggerate the effect when applied without levelling agents in the dyebath.

Although the chrome dyes and chrome complex dyes are used extensively for wool dyeing, the development of machine-washable wool has brought even higher demands for wet fastness, and this is usually achieved using reactive dyes.

### ***Reactive dyes for wool***

Some of the most stringent demands of quality arise with the coloration of shrink-resist-treated wool that may be washed in a domestic washing machine. Much of the wool so designated is produced using aftertreatments that deposit polymeric compounds on the fibres. These have the effect of reducing the wet fastness of most conventional wool dyes, just where greater resistance to



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wet treatments is needed. This deficit can be effectively covered by the use of dyes chemically identical with, or similar to, the reactive dyes intended for cellulose (see page 91).

Reactive dyes are necessarily applied to cellulosic fibres under alkaline conditions, but alkaline conditions are usually inappropriate for wool because of the sensitivity of the disulphide crosslinks (page 54). Fortunately, the chemical nature of the functional groups in wool enables the reactive dyes to react with the fibres under mildly acidic conditions. Some are based on levelling acid dye molecules and others on 1:2 metal-complex dyes. Particular care is needed to achieve level dyeings because, once the dye has reacted with the fibre, migration is clearly impossible. Furthermore, any unfixed dye remaining on the fibre still remains sufficiently substantive to cause staining problems during use, and particular care is needed with washing-off after dyeing. Additives are included in the dyebath to avoid the danger of producing 'skittery' dyeings (an undesirable speckled effect arising from differences in colour between adjacent fibres or portions of the same fibre). The use of reactive dyes is generally limited by their cost, which is high compared with that of other wool dyes.

### **Selection of dyes for cellulosic fibres**

The widespread use of natural cellulosic fibres such as cotton and linen, and also of regenerated cellulosic fibres, maintains a demand for a broad range of shades and different standards of fastness properties. For example, for many uses such as high-quality curtaining, military and naval uniforms and high-class gabardines good fastness to light is essential, but for others fastness to bleaching may be more important. Such a need may arise when bleaching is required to clean uncoloured parts of the design after weaving fabrics that incorporate both dyed and undyed yarns. Dyes may also require resistance to the bleaching ingredients included in commercial detergent preparations. For sewing yarns and furnishings intended for the cheaper end of the market, however, the demands on fastness properties are less stringent.

This diversity of requirements has led to the development of several different coloration principles for cellulosic fibres. There are water-soluble dyes applied by a one-bath process without the use of mordants (*direct dyes*), water-soluble dyes that form a chemical linkage with the fibre (*reactive dyes*) and water-insoluble pigments that are applied as water-soluble precursors which are converted to the insoluble pigment after diffusion into the fibre (*vat dyes*, *azoic dyes* and *sulphur dyes*). Here each dye class will be discussed in turn.



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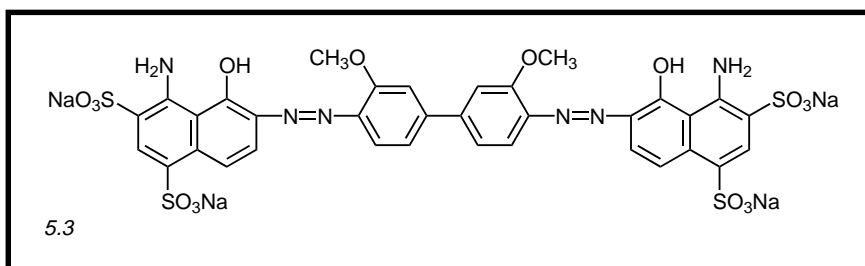
## Direct dyes

The discovery by Böttiger of the dye Congo Red in 1884 was a landmark because this was the first dye to be used for colouring cellulose by a simple one-bath operation (i.e. directly) in the absence of a mordant; hence the term 'direct dye'.

### *Nature of direct dyes*

The molecules of direct dyes are similar in structure to those of acid dyes but they are larger; structure 5.3, the dye Sky Blue FF (CI Direct Blue 1) is an example. They conform to the general formula  $R_1-N=N-X-N=N-R_2$ . It is their size that distinguishes them from acid dyes and makes them substantive to cellulose. Their attachment is through both hydrogen bonds and van der Waals

forces and, as we have seen (page 81), the intensity of the latter increases with increasing molecular size. Their hydrogen bonding capability is



also aided by their long flat molecular structure which enables them to lie along a cellulose chain in register with hydroxyl groups.

The function of the sulphonate groups is limited to conferring water solubility on the molecule because, unlike wool, cellulose contains no cationic groups with which the coloured dye anions can form electrostatic linkages.

Compared with other classes of dye for cellulose the wet fastness properties of direct dyes are usually poor and where repeated washing of the dyed fabric is likely, as with lingerie, they are generally of use in pale shades only. A variety of aftertreatments is available to make the dye on the fibre less soluble in water to give improved fastness performance (page 106), but unfortunately such improvements are accompanied by a change of shade or reduced fastness to light.

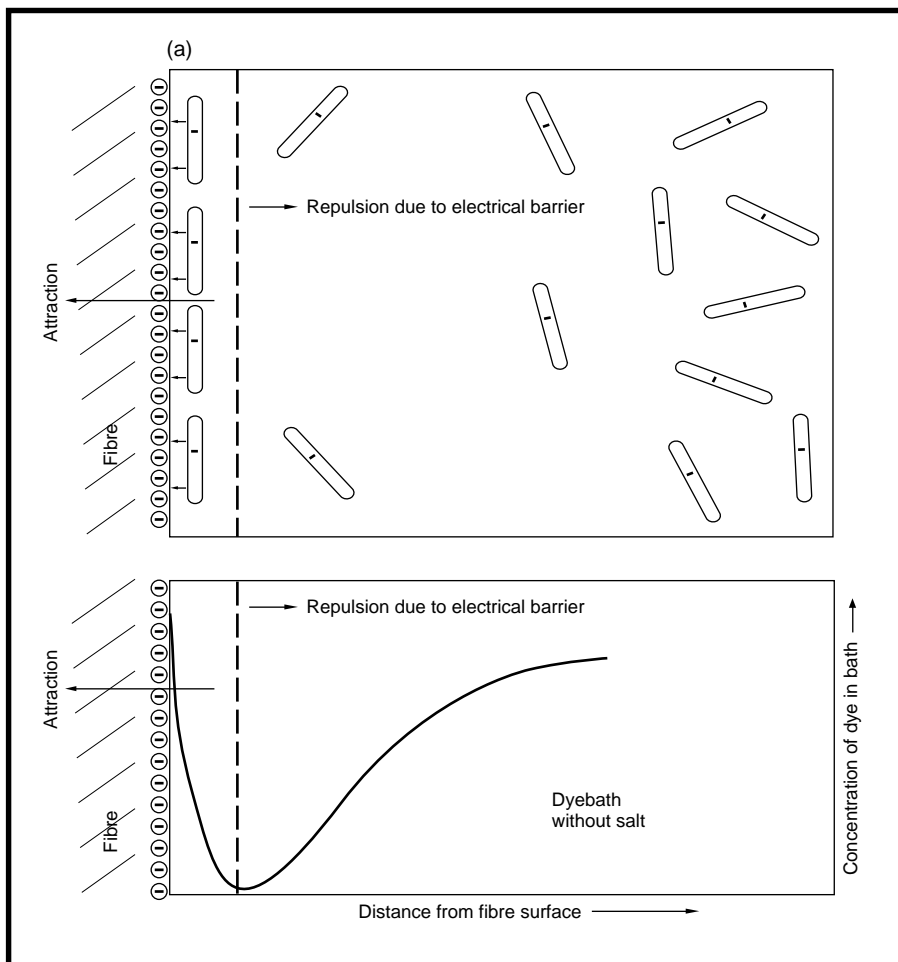
The merits of direct dyes are their simplicity of application, the wide range of shades they can provide, and a cost that usually compares favourably with other alternatives. As a consequence, direct dyes are found in many different outlets, including cotton and viscose dress fabrics, sewing yarns, book cloths, pile fabrics and shoe canvas.

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As with acid dyes, selection is aided by placing the dyes in groups with similar dyeing properties. Often a mixture of dyes is needed to produce the required colour, and sometimes the use of dyes from different groups cannot be avoided. In such cases the dyeing method is chosen to suit whichever component is most difficult to dye level.

### *Application of direct dyes*

Direct dyes are usually applied by bringing the dyebath to the boil gradually and holding it at this temperature whilst the dye diffuses into the fibre. In the complete absence of electrolyte (i.e. with a



**Figure 5.1** The effect of salt on dye distribution at the fibre surface: (a) in the absence of salt, the initial adsorption of dye anions increases the negative charge on the fibre surface, and hence other dye anions are repelled; (b) (overleaf) in the presence of salt, cations redistribute around the electrical barrier to neutralise the charge and so allow other dye anions to reach the fibre surface, whence they can diffuse into the body of the fibre

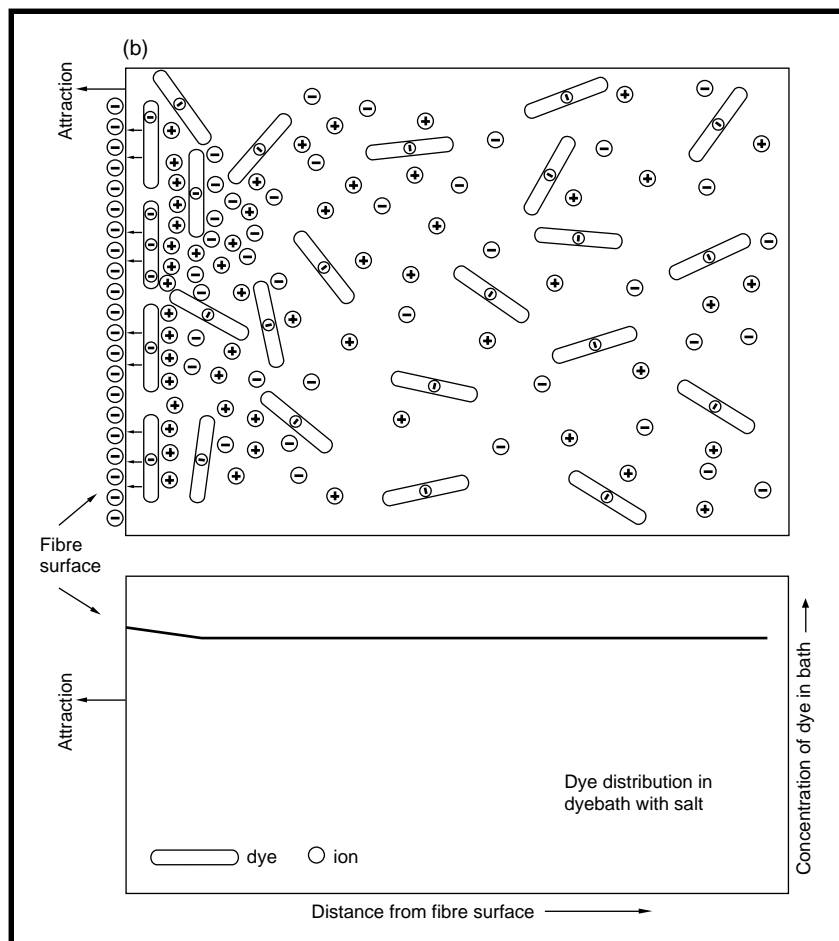


Figure 5.1(b)

mersed in water. In the absence of other influences the consequence is repulsion of other dye anions near the surface (Figure 5.1 (a), page 89). Meanwhile, the positive sodium ions originating from the dye are attracted towards the negatively charged surface, but their concentration is insufficient wholly to neutralise the negative surface charge. Other dye anions can approach the fibre only when the charge is completely neutralised, and this occurs when further electrolyte is deliberately added to the dyebath. This is why the application of direct dyes always involves common salt (sodium chloride) or Glauber's salt (sodium sulphate) as a component of the dyebath (Figure 5.1 (b)).

In practice the rate of dyebath exhaustion is controlled by both the addition of electrolyte and the regulation of dyebath temperature. Individual dyes vary in their response to electrolyte: the more sulphonic acid groups there are in the dye molecule, the greater will be the effect of electrolyte and the greater the care needed to obtain level dyeings.

chemically pure dye) some direct dyes will not dye cellulose at all, and all commercial direct dyes are absorbed much more readily if salt is added to the dyebath. This is because the dye anion is substantive but the sodium cation is not. The greater substantivities of the dye anions initially lead to their preferential adsorption, but once they start to be adsorbed their negative charge adds to that already acquired by the fibre when it is first im-

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Direct dyes are classified into three subgroups, according to the effect of changes in electrolyte concentration and dyebath temperature on their dyeing properties. The three groups of the SDC classification are as follows.

- (a) Group A contains those dyes that can be applied easily, with electrolyte present from the start of dyeing. They are referred to as *self-levelling* dyes and are often used for the shading of faster dyes in hot dyebaths.
- (b) Group B contains those dyes for which the rate of addition of electrolyte throughout the dyeing process must be regulated in order to control dyeing. They are called *salt-controllable* dyes.
- (c) Group C contains those dyes for which regulation of both the rate of increase of dyebath temperature and the addition of electrolyte are essential for adequate control. Dyes in the latter group all possess very high substantivity, even in the presence of only small amounts of salt. Because of their marked additional dependence on the dyebath temperature, they are referred to as *temperature-controllable* dyes.

This scheme of classification is appropriate for the dyeing of both natural and regenerated cellulosic fibres, but since direct dyes are more substantive to regenerated cellulosic fibres than to cotton, there is a corresponding increase in the difficulty of producing level dyeings. A practical advantage may be taken of this difference by producing two-tone effects in the dyeing of cotton/viscose blends.

### **Reactive dyes for cellulose**

Until 1956 the only known way of producing dyeings of very high wet fastness on cellulosic fibres was through the deposition of water-insoluble pigments within the fibre. But at this time I D Rattee and W E Stephen discovered that dye molecules containing certain chemical groups (*reactive groups*) could react chemically with cellulose under alkaline conditions. Thus for the first time it became possible to make a dye react with the fibre and become part of it, rather than remaining as an independent chemical entity within the fibre.

Rattee and Stephen's discovery was followed by the introduction of the Procion range of dyes by ICI, which illustrated the technical possibilities of producing bright shades of high fastness through a variety of application methods. Since then many similar dyes have become available. The



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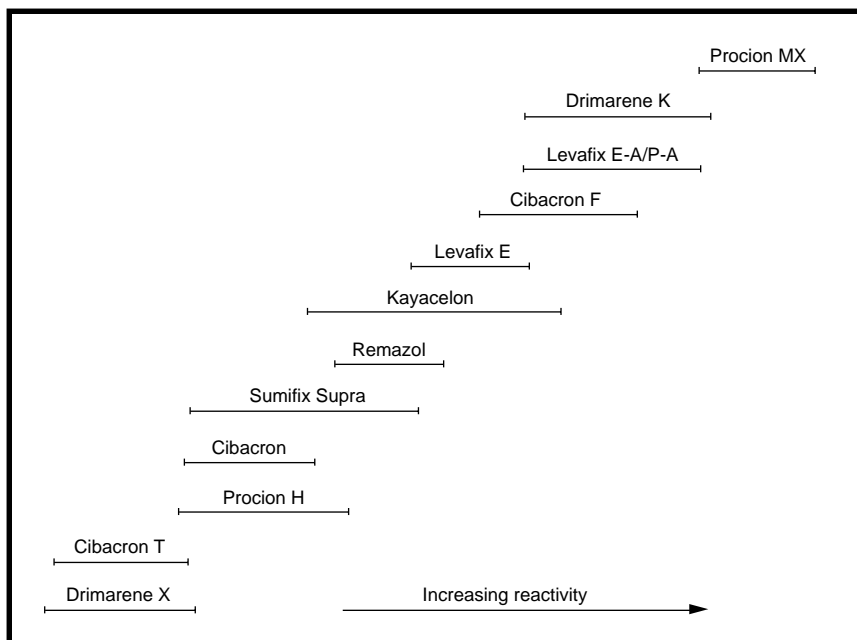


Figure 5.2 Relative reactivities of reactive dyes for cellulose fibres

current ranges of reactive dyes include many that have a broad spread in their level of reactivity and substantivity. Some examples are shown in Figure 5.2, in which their respective levels of reactivity are compared. Since their introduction these dyes have played a dominant role in the dyeing of cellulosic

fibres and, at the time of writing, their usage is still growing (Table 5.2).

Many reactive dyes possess a resistance to daylight previously only associated with vat dyes, and this is reflected in their use for top-quality curtains, furnishings and awnings. They also contribute to the colour quality of many domestic goods that require frequent washings, such as towellings, and are used extensively for shirtings, tapes, ribbons, dress goods and knitted sportswear; the last-named accounts for around 40% of the reactive dye market.

Table 5.2 World consumption of dyes for cellulosic fibres by dye class

Dye class	Consumption (tonne $\times 10^3$ /year)		
	1973	1979	1988
Direct	75	74	74
Vat	55	57	48
Sulphur	108	100	90
Azoic	29	29	26
Reactive	23	42	60
Total	290	301	300

Source: ICI Colours and Fine Chemicals, internal estimates

*Nature of reactive dyes*

The type of reactive group in a reactive dye molecule determines the level of its reactivity, whilst its substantivity is governed by the chromophore; both properties are equally important in controlling

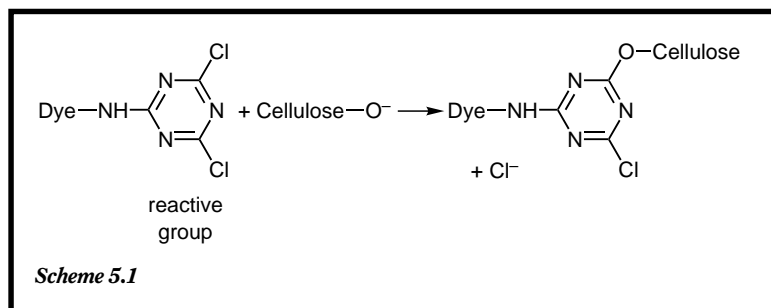
## 5. THE SELECTION, CLASSIFICATION AND APPLICATION OF DYES

the quality of dyeings. The reaction of a reactive dye with cellulose is shown in Scheme 5.1. The cellulose reacts as the cellulose anion, which is formed under alkaline conditions only. That is, the dye–fibre reaction only takes place when alkali is added to the dyebath.

The molecules of reactive dyes are smaller than those of direct dyes, and their smaller size is accompanied by a correspondingly lower substantivity. The molecules of direct dyes are made deliberately large so as to

build up the physical attraction between fibre and dye, thus making them more substantive. Much smaller molecules may be suitable for use as reactive dyes because one covalent bond is about thirty times as strong as one van der Waals bond.

As the size of a dye molecule becomes larger, the colour it imparts becomes duller. Reactive dye molecules therefore confer very bright colours to dyeings because their molecules need be no larger than those of simple acid dyes.



### ***Selection of reactive dyes***

Very many reactive dyes are now commercially available, with a variety of reactive groups. Their simplicity of application and broad spread of reactivity and substantivity makes them very versatile in application. But, as with other classes of dye, the quality of their dyeings depends upon careful dye selection. Appropriate levels of reactivity, substantivity and rate of diffusion are needed for the method of application best suited to the goods in hand. Indeed the dyeing of reactive dyes may be described quantitatively in these terms, but usually a simpler empirical representation is more appropriate on the shop floor.

The two essential stages in the application of reactive dyes are (a) diffusion of dye into the cellulose fibre, and (b) reaction between the dye and cellulose. The former is controlled by varying the dyeing time, the dyebath temperature and the salt concentration, and the latter is achieved by the selection of an appropriate alkalinity (pH).



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### ***Substantivity of reactive dyes***

The low substantivity of the reactive dye molecules before fixation by alkali permits very easy levelling, but once they react with the fibre they cannot migrate further and they become resistant to normal domestic washing treatments. Inevitably, once alkali is added to the dyebath, reaction of the dye with cellulose begins. At the same time, however, the dye begins to react with water (*hydrolysis*), and the hydrolysed dye becomes a nuisance. It retains its substantivity but not its reactivity, and needs to be removed in the final washing-off. This situation is usually expressed in terms of the 'efficiency' of a dye or dyeing process, which is represented as a ratio of the amount of dye chemically combined ('fixed') to the amount of dye applied. This efficiency can never reach unity, because the presence of hydrolysed dye cannot be avoided even if the conditions could be adjusted to give 100% take-up (exhaustion) from the dyebath.

### ***Dyeing temperature and reactivity***

The decreased substantivity caused by raising the dyeing temperature aids both levelling before the addition of alkali and washing-off the unfixed dye at the end of the process. A great deal also depends upon the reactivity of the dye, however.

There are two groups of reactive dyes, differing in their level of reactivity. The first includes highly reactive dyes that can be applied efficiently at temperatures as low as room temperature; these are referred to as *cold-dyeing* reactive dyes. Dyes of the second group are approximately 1500 times less reactive and require temperatures of 80–100 °C for fixation; they are *hot-dyeing* reactive dyes.

The reactivity of a particular dye can be increased further by (a) increasing the alkalinity of the dyebath (i.e. increasing the pH value), and (b) raising the temperature. Although the initial discovery of reactive dyes held a promise of dyeings carried out at room temperature, difficulties with obtaining well-penetrated dyeings, free from skitteriness and streakiness, were encountered with tightly woven fabrics dyed to heavy mixture shades. Such fabrics include mercerised cotton fabrics containing highly twisted yarns, as used for rainwear, for instance. Packages of mercerised or densely wound yarns presented similar difficulties. In such cases a raised dyebath temperature is needed to aid penetration and hence level dyeing. Higher temperature increases the reactivity of the dye, which itself carries a danger of unlevel dyeing; this in turn requires further control of reactivity



## 5. THE SELECTION, CLASSIFICATION AND APPLICATION OF DYES

through a reduction in the pH of the dyebath. Thus substantivity and reactivity are manipulated together to control the quality of dyeings.

### *Effect of salt concentration*

In a neutral solution reactive dyes are anionic in character (like direct or acid dyes), but their substantivity is low; it is of course this lower level of substantivity that confers the excellent levelling properties on reactive dyes. Compensation is made for this in batchwise dyeing by using much higher salt concentrations than are used with other dyes for cellulosic fibres. The lowered substantivity persists until the reaction between dye and fibre is initiated by the addition of alkali to the dyebath. Once fixation has taken place, however, mistakes cannot be rectified.

### **Reactive dyeing processes**

The level of substantivity required for a particular coloration process depends on the amount of water required in relation to the mass of fabric, i.e. the *liquor-to-goods ratio*, often just called the 'liquor ratio'. With a liquor ratio of 50:1, 50 kilograms (i.e. 50 litres) of dyebath will be required for every kilogram of textile. In some methods a suitable quantity (batch) of goods is fully immersed in liquor throughout the whole process, and the liquor ratio can then be between 100:1 and 30:1. In other procedures the fabric is passed through the liquor repeatedly and the ratio is generally lower, around 20:1 to 5:1 depending on the particular machine used. Usually the higher the liquor ratio, the higher is the substantivity required to produce a good colour yield in a reasonable time.

Not all textile goods are prepared in small batches. Sometimes thousands of metres of identically coloured fabric may be needed, in which case it is impossible to immerse the entire bulk of the goods in one vessel. It is then more economical to resort to methods that allow a continuous movement of material through the entire process rather than split it up into more manageable batches. Such processes are designed to proceed from start to finish without interruption, and are appropriately referred to as continuous processes. For this purpose the fabric is passed through a trough containing the solution of dye and alkali (*padding*). It is then passed between the pressurised rollers of a padding mangle, a process in which the fabric becomes uniformly impregnated and the surplus liquid is removed. The continuous movement then carries the fabric into either a dry- or a



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steam-heated chamber to bring about fixation. As it emerges from the chamber it passes through the washing-off range and it is finally dried.

For continuous processes rapid washing-off is essential, and this is favoured by using dyes of a lower substantivity. This also avoids premature exhaustion of dye from the padding liquor during the time the fabric is passing through. If exhaustion were allowed to happen too rapidly, the fabric would develop a deeper shade at one end than at the other, a phenomenon known as 'tailing'. A low substantivity is also advantageous in textile printing (see page 126).

### **Control of batchwise dyeing**

The rate of reaction between dye and cellulose is proportional to the concentration of dye in the fibre. Consequently the higher the substantivity, the greater the exhaustion and the quicker the reaction with cellulose when the bath is made alkaline. The need in batchwise dyeing methods is therefore to strike a balance between achieving the most efficient fixation, the most level dyeing and the most complete removal of hydrolysed dye.

As we have seen, there is room for control in deliberately reducing the substantivity by raising the temperature or by changing the reactivity of the dye through adjustments in pH. Conversely the substantivity can be increased by increasing the concentration of electrolyte before alkali is added to the dyebath. There are practical limits to the degree of control that can be exercised through each expedient, however, and as a general rule dyes of high substantivity can be induced to provide good yields by most methods involving the use of water. Dyes of low substantivity, on the other hand, give good yields only in padding operations. These are described below, and in further detail in Chapter 6.

The general principle of batchwise or exhaust dyeing with reactive dyes is to encourage as much dye as possible to move into the fibre over a period of 30–45 minutes by adding a high concentration of salt to the neutral dyebath. Consequently most of the dye is exhausted on to the fibre before the alkali is added, thus providing the best possible conditions for fixation before the dye–fibre reaction is initiated. Once the levelling process is complete, alkali is added and fixation continues for a further 30–60 minutes.

For highly reactive dyes, i.e. the cold-dyeing dyes, the temperature of dyeing can be set between 30 and 60 °C depending on the type of fabric and the strength of alkali. Typically, a pH of 10–10.5 and a dyeing temperature of 40 °C are used; fixation is achieved using sodium carbonate as



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alkali. The pH is modified to 9.9–10.0 by using sodium hydrogencarbonate (bicarbonate) when temperatures of 60 °C become necessary for certain fabric constructions. During fixation hydrolysed dye also becomes exhausted on to the fibres. To eliminate future staining which this loosely bound dye would otherwise cause, all reactive dyeings are subjected to a thorough washing-off process at the end of the dyeing cycle.

The method used with the hot-dyeing dyes is in principle identical, the difference being the use of a dyeing temperature between 65 and 90 °C and stronger alkali (i.e. a higher pH, generally 10.5–11.0); fixation is again with sodium carbonate.

A further variable is the liquor ratio, which in batchwise application can vary from 30:1 for yarn dyeing to 5:1 for jig dyeing (see page 117).

Clearly the mass of dye required for a given depth of shade is independent of the liquor ratio, and the concentration of dye used when dyeing at a low liquor ratio will be higher than for a high liquor ratio. A given mass of dye dissolved in a smaller volume of water will give a higher exhaustion. The choice of dyes for low-liquor-ratio dyeing may include those with a medium to low substantivity, whereas higher-substantivity dyes are generally employed at high liquor ratios. The high-fixation Procion HE dyes of ICI, for example, are particularly effective at high liquor ratios because they contain two reactive groups in each dye molecule. Hence they have double the chance of reacting with the cellulose before becoming hydrolysed.

Due allowance is also made for the kind of cellulosic fibre; the rate of dyeing decreases in the order: viscose fibre > polynosic fibre > mercerised cotton > linen.

The batchwise dyeing cycle is represented diagrammatically in Figure 5.3.

### *Control of the pad-batch process*

The pad-batch process is essentially a semi-continuous one. A notable feature of the pad-batch process for reactive dyes is that a pad mangle is the only equipment required. Dye and alkali are padded from the same bath, the fabric is rolled on to a perforated or unperforated beam, covered with a plastic sheet to prevent drying out, and stored (batched) for long enough to allow dye diffusion and fixation to take place. The coloration process is then completed by washing the dyed fabric free of alkali and loose dye.

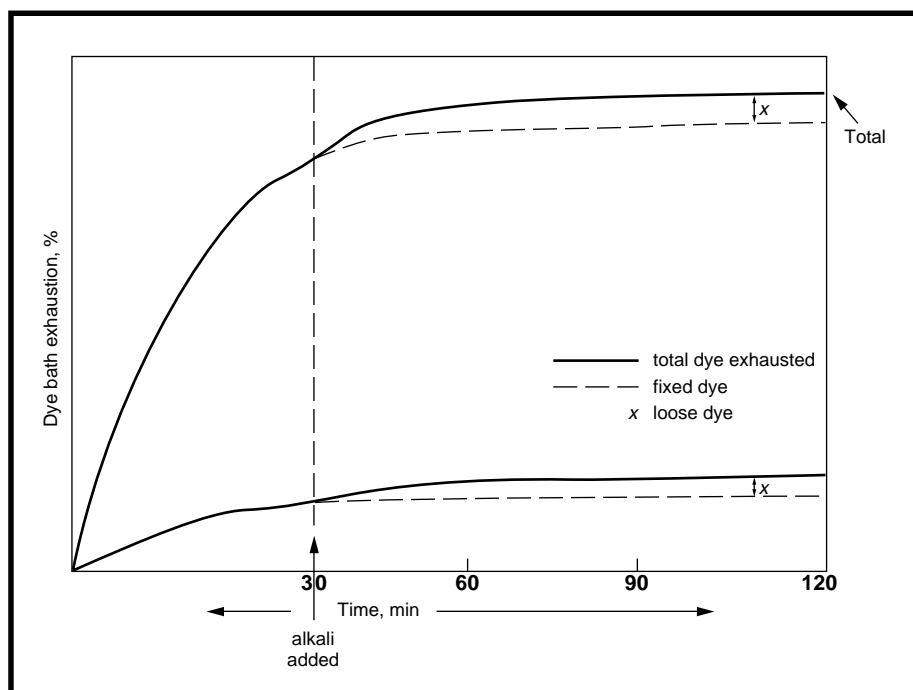
If the fabric was originally batched on a perforated hollow beam, it does not even need to be removed for washing since all the unfixated dye and chemicals can be washed away by pumping water



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**Figure 5.3** Rate-of-dyeing curve for a reactive dye

through the beam. Since the hollow beam is closed at one end, water is forced through the perforations into the bulk of the fabric. Within the fabric the slight positive pressure forces direct replacement of the existing dye liquor held between individual fibres with fresh water, thus flushing out the surplus dye and chemicals. This requires much less water than the conventional washing-off procedure, in which the fabric is passed through a large volume of water and which relies on the removal of loose dye and chemicals by water passing over the fabric surface.

### ***Control of dye fixation***

The pad-batch process is usually carried out at room temperature, and therefore the pH of the pad liquor is the most important variable in its control. Variations in pH of the padding liquor are used to accommodate variations in the batching time needed for penetration and fixation. Flexibility is essential for various technical reasons. For example, the greater resistance to the penetration of aqueous solutions offered by a tightly woven fabric at room temperature dictates that a longer batching time is required, but this is accompanied by a greater danger of premature hydrolysis; consequently where longer batching times are used the alkalinity is reduced. The conditions used for the cold-dyeing dyes are usually a 2 hour batching period for dye liquor at of pH 10.5–11.0 (using

## 5. THE SELECTION, CLASSIFICATION AND APPLICATION OF DYES

sodium carbonate) and 24 hours batching, or even longer, for a pH of 10 or below (using sodium hydrogencarbonate or sodium hydrogencarbonate/carbonate mixtures).

With the less reactive hot-dyeing reactive dyes a stronger alkali is called for and a pH as high as 12–13 may be required. Sodium hydroxide (caustic soda) is used as alkali, together with batching times of up to 48 hours. These conditions lead to a greater loss of dye by hydrolysis, and the colour yield is usually lower than that obtained with cold-dyeing types. Furthermore, the low colour yield cannot be counteracted by the use of the high-fixation Procion HE dyes because their high substantivity and enhanced fixation lead to ‘tailing’.

Speeding up the process is possible by batching at between 50 and 70 °C with an additional piece of equipment called a pad-roll machine. This gives improved penetration, diffusion and more rapid fixation but has attendant technical problems. Variation in temperature across the width of the fabric, due to cooling of the edges of the roll, can bring uneven fixation across the width, a phenomenon called ‘listing’. Dye may also migrate during the batching because of partial drying of the fabric from the edge. In general, therefore, the dyes chosen for application by the pad-batch process are those suited to cold batching.

### **Control of continuous dyeing**

The simplest way of applying a uniform distribution of dye on a fabric is by a padding method, outlined above. The effort is minimal and the method is efficient in terms of dye consumption, levelling and water consumption, the liquor ratio being about 1:1.

Although padding is a mechanically simple operation, care has to be taken to avoid loss of quality of the dyed fabric due to ‘tailing’. The effect can become serious with dyes of high substantivity. Consequently dyes of lower substantivity, which do not exhaust too readily, are preferred for padding operations. It is only in continuous methods that dyes of low substantivity give a high colour yield.

Padding operations are the first step for many of the continuous methods of application of reactive dyes in which the whole process is completed from start to finish without a break. After the initial padding stage the method of fixation varies but, whichever sequence of operations is chosen, the aim is still to allow dye to diffuse quickly prior to fixation. Conditions of fixation encompass the use of dry heat at up to 200 °C or heating by pressurised steam. Usually the levels of fixation achieved are higher than those obtained by batchwise methods.



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The rapid outward movement of water in dry heat fixation tends to cause low-substantivity dyes to migrate to the surface of the fabric with the evaporating water. Consequently various proprietary pad liquor additives may be incorporated to increase the viscosity. The problem may be avoided by choosing dyes of higher substantivity.

### *The pad(alkali)-dry process*

A padding process is the first step in the pad-dry sequence. The padding liquor contains sodium carbonate as alkali, sodium alginate as a migration inhibitor and a wetting agent to ensure rapid and efficient impregnation of the fabric by the pad liquor and dye. Since the volume of liquid is small, a high concentration of dye in the pad liquor is required to produce deep shades. The attendant problems of inadequate dye solubility can be counteracted by adding urea to the padding liquor. The reactivity of the cold-dyeing dyes allows fixation within a few minutes or less in hot air at 100–200 °C. Temperatures of 200 °C with urea and sodium bicarbonate are used for the corresponding pad(alkali)-bake process for hot-dyeing dyes. Persistent migration at these higher drying temperatures can often be avoided by introducing an intermediate drying stage at a lower temperature. Consequently a pad(soda ash)-dry-bake process is also available that complements the pad(bicarbonate)-dry process for cold-dyeing dyes.

### *Pad(alkali)-dry-steam process*

Fixation by steam heating is also accompanied by a predrying process, which for cold-dyeing dyes becomes a pad(bicarbonate)-dry-steam sequence. For hot-dyeing dyes a pad(soda ash)-dry-high-temperature-steam sequence uses superheated steam at 220 °C to accelerate fixation.

The oldest sequence of all is a double padding system, i.e. a pad(dye)-pad(alkali)-steam process, in which a fixation time as brief as around 5–10 seconds is possible.

Principles similar to those that underlie pad dyeing methods are also appropriate for the fixation of reactive dyes in textile printing.

## **Dyes held as insoluble particles inside the fibre**

The ultimate fastness to wet treatments on cellulosic fibres is obtained when water-insoluble coloured molecules become trapped mechanically inside the fibre, because diffusion out of the fibre



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during washing is then impossible. This principle underlies the action of several classes of dye, including vat dyes, sulphur dyes and azoic dyes. There are also the so-called ingrain dyes bearing the Alcian and Phthalogen trade marks. These are limited ranges noted particularly for their unique turquoise colour, provided by the remarkably stable copper phthalocyanine chromophore. Further discussion here is limited to the more extensive ranges of colours provided by the vat, sulphur and azoic classes.

### **Vat dyes**

Vat dyes are used in the dyeing and printing of all types of cellulosic fibre, and also of blends of cotton with polyester. In their coloured form they are insoluble pigments, so their application depends on reversible reduction–oxidation (redox) reactions (page 42). In the dyebath the pigment is converted into a water-soluble form using a strongly alkaline solution of a powerful reducing agent. This forms the sodium ‘leuco’ compound of the dye, which is soluble in water but often different in colour from the original pigment. It is then allowed to dye the cellulose in this water-soluble form; once exhaustion is completed the leuco compound is oxidised to the coloured form.

#### *Chemical nature of vat dyes*

The large majority of vat dyes are based on the anthraquinonoid or the indigo (or thioindigo) chromophores; indigo, one of the oldest dyes still in use, remains popular through the wide use of indigo-dyed denim. Several of the anthraquinone dyes are complex polycyclic quinones (Appendix 1), and they all possess two carbonyl groups ( $>C=O$ ) linked by alternate single and double bonds in a conjugated chain. This molecular arrangement is responsible for the easily reversible redox reactions on which the application of vat dyes depends.

In earlier centuries, when all textile colorants were obtained from natural sources, indigo plants were steeped in a large vat. It is from this ancient vatting process that the term ‘fermentation vat dyes’ is derived. Fermentation converts one of the plant constituents into the soluble leuco dye, which diffuses out of the plant. The replacement of natural by synthetic indigo at the end of the nineteenth century gave the impetus to research on other syntheses, and many synthetic vat dyes have since followed.



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Synthetic vat dyes are costly because they are difficult to prepare, and so their use is usually directed to the higher-quality fabrics. Nevertheless, they are widely used and noted for their high fastness to light, in the dyeing of fabric for uses such as awnings, curtains, upholstery, military and naval uniforms, and high-quality gabardines.

High fastness to bleaching is another strong point of the anthraquinonoid group. This is exploited in the production of patterned fabrics from vat-dyed yarns in which the white areas of the pattern can be safely bleached out after weaving.

Anthraquinonoid vat dyes are widely used in the manufacture of, for example, good-quality shirtings, tablecloths, towels, sportswear, high-quality overalls, fabrics for women's and children's clothing and tropical suitings, and yarns and effect threads where repeated washing will be required. With careful dye selection, the use of vat dyes allows materials to be prepared with a guarantee against fading. A limitation, however, is that the range lacks scarlet, maroon and wine shades.

### *Application of vat dyes*

Both the extent of reduction and the rate at which equilibrium between the reduced and oxidised form is achieved are of practical significance. Vat dyes vary in the speed with which they undergo reduction. The most common reducing agent used for the reduction of vat dyes is sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), which is capable of completely reducing even the most stable of vat dyes. As a result any difficulties in vatting can be overcome by raising the vatting temperature, increasing the concentration of reducing agent or prolonging the vatting time. The vatted dye must be kept in a strongly alkaline solution, because its leuco form is an insoluble acid. If, instead of being formed as its water-soluble sodium salt, it is formed as the free acid, it will not readily oxidise to the coloured form.

There are still some application methods in which reduction and adsorption on the fibre take place rapidly and almost simultaneously. Under these conditions the rate and extent of reduction can be decisive factors in the dyestuff choice – for example, in textile printing. Premature oxidation of the leuco compound in the print paste must also be avoided during both storage and steaming. This condition is usually met by using as the reducing agent sodium formaldehyde sulfoxylate (Formosul), a compound that is fairly stable in air at room temperature and develops the necessary action during steaming.



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Variables such as pigment particle size and crystalline form can affect the rate of reduction, but these are controlled by the dye manufacturer. Consequently the colourist needs to concentrate only on the temperature and the concentration of reducing agent.

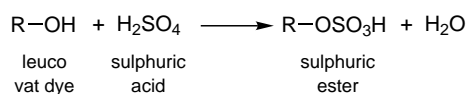
Leuco compounds can be applied by batchwise methods similar to those used for other dye classes, but there are difficulties in obtaining level dyeings. The necessary high concentrations of sodium hydroxide and reducing agent affect the exhaustion, just as the addition of salt does in direct or reactive dyeing. The difference is that the option of reducing the concentration of the additions is not available, because they are needed to form the leuco compound. Serious levelling problems can be lessened by raising the temperature of dyeing and then cooling to obtain satisfactory exhaustion, or by using a dyebath auxiliary that restrains the rate of exhaustion. A different approach is to use specially formulated stable dispersions of the pigment, in which form they are evenly distributed on the fabric by padding (*pigment padding*), followed by working the padded fabric through a solution of caustic soda and sodium dithionite on a jig. Pre-pigmentation can be carried out using package, jig, winch or beam dyeing machines (described in Chapter 6), provided specially formulated vat dyes are used. Once the pigmentation is completed, sodium hydroxide and sodium dithionite are added to the dyebath to reduce the pigment and allow the leuco dye salt to diffuse into the fibre.

Oxidation in air or in solution is then used to regenerate the pigment. A soaping treatment is given to the fabric at the end of the dyeing process; this is essential, both for cleaning the dyed fabric and for developing the final shade. In some cases a change in the crystalline form of the dye accompanies the change in shade.

### Solubilised vat dyes

The need to reduce vat dyes before use makes their application a cumbersome process. Although it is possible to isolate the reduced form of the dye, it is too readily oxidised in air for the manufacturer to provide

the dyer with the leuco compounds. It is possible, however, to convert the leuco acid into the leuco ester, a derivative that has greater resistance to oxidation and greater solubility in water. Such esters can be formed by the reaction of a hydroxyl group of a leuco acid with sulphuric acid, forming a sulphuric ester (Scheme 5.2). The sodium salts of such esters are stable and can be stored until required for use. Since the ester group is only weakly attached to the rest of the dye molecule, it is



*Scheme 5.2*



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easily removed by the action of sodium nitrite in dilute sulphuric acid. The regenerated leuco compound may then be oxidised back to the pigment form.

Solubilised vat dyes are less rapidly taken up than are the more conventional vat dyes and are mainly used for the production of pale shades. As with ordinary vat dyes, application under alkaline conditions is essential, thus eliminating wool from the list of possible substrates because alkaline conditions modify the wool fibres. The low uptake and higher cost of solubilised vat dyes make them uneconomical for deep shades, however, and for these normal vat dye alternatives have to be used.

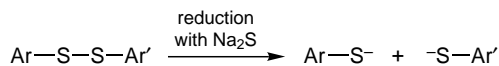
An interesting property of solubilised vat dyes is their sensitivity to light in the solubilised state. This is used to produce 'photographic' prints on fabric. Fabric dyed by padding (page 95) with one of these dyes may be placed on a suitable support with a photographic negative laid on its surface and exposed to ultra-violet light. Where the light penetrates the negative and reaches the surface of the dyed fabric the dye becomes converted to the insoluble pigment, and after washing the treated fabric free of dye a positive image remains (Plate 5).

## Sulphur dyes

Deposition of insoluble pigments inside fibres may be achieved more cheaply using sulphur dyes, but with these the shade gamut is restricted to black, mauves, olives, bordeaux and reddish-browns. One of the earliest and best-known sulphur dyes is CI Sulphur Black 1, which is a popular black with good fastness properties still in use today.

Like vat dyes, sulphur dyes are reduced and applied as soluble leuco compounds that need to

be kept under alkaline conditions, but sulphur dyes need only sodium sulphide to act as both alkali and reducing agent. A simplified version of the reaction is represented in Scheme 5.3. The structure of the chromophore of sulphur dyes is complex and unknown. Again like vat dyes, these



Scheme 5.3

dyes cannot be applied to wool without damage to the fibres due to the action of sodium sulphide on the cystine crosslinks (page 54). After exhausting the dyebath for approximately 1 hour at 60–90 °C the fabric is thoroughly rinsed and exposed to the atmosphere, where oxidation generates the mechanically entrapped insoluble pigment.

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One disadvantage of certain sulphur dyes (although, strangely, this problem appears to arise with the black shades only) is that dyed material stored under conditions of high humidity and temperature can lose its natural strength. This is because inadequate washing-off after dyeing can lead to the slow generation of sulphuric acid in the fibre, arising from the presence of sulphur.

Sulphur dyes are used mainly in the dyeing of cellulose fabrics and in blends of cellulose with polyester, nylon and acrylic fibres. Typical applications are for heavy drill fabrics, corduroys, overalls, denims, awnings and canvas. Limited quantities are also consumed in the coloration of silk, paper and, more widely, leather.

### **Azoic colorants**

In the early development of synthetic dyes a considerable impetus to progress came with the discovery by Peter Griess in 1858 that aromatic amines could be converted to *diazonium compounds* (page 35). These react readily with certain other compounds known as *colour couplers* or *coupling agents*, to produce insoluble dye particles within the fibre. Some years later, in 1876, Otto N Witt produced chrysoidine, the first commercially successful azo dye.

The commercial use of the colour coupling reaction had to wait until some years after the initial discovery when Read, Holliday and Co. described a process in which a 'coupler' was applied to cotton fabric, and the fabric was then dried and passed through an ice-cold solution of a *diazonium salt*. As a result, an azo dye was synthesised within the fibre.

Both coupler and diazonium salt are relatively small molecules and can easily penetrate the pores of cellulosic fibres, even in the cold. Once the dye is formed, it is trapped in the fibre. In subsequent soaping the dye particles aggregate into larger particles, giving dyeings with good wet fastness. Care must be taken, however, to ensure that too much insoluble dye does not form at the fibre surface, as otherwise the colour can be removed by abrasion.

A range of both colour couplers and diazonium salts is available, giving a variety of different colours. A full range of bright hues is possible with high fastness ratings to light, wet treatments and bleach, although relatively few members of the range lie in the blue-green sector of the colour gamut.

Earlier azoic dyeings were inconvenient to carry out because the dyer had to make and use all the diazonium salt solutions he needed in the winter, when ice was readily available (hence the name 'ice colours') – otherwise the very reactive diazonium salts decomposed. Later dye manufacturers



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were able to produce stabilised diazonium salts called Fast Salts, so avoiding the necessity of the ice-cold step. Instead the Fast Salts can be dissolved in water and applied to fabric that has previously been impregnated with a coupling agent. The range of substantivities of these agents covers products suitable for both printing and dyeing. Low-substantivity coupling agents are useful for printing applications, because after printing with the Fast Salt the unused coupling agent can readily be washed off to give a white background. Alternatively, level dyeing of a coupler of higher affinity will give a fabric that can be passed through the Fast Salt solution without bleeding-off.

For greater convenience a mixture is available that contains a coupler and a substance that generates a diazonium salt only under regulated conditions, thus providing the possibility of a one-bath process. Once the agents are exhausted on to the fibre, the addition of acid to the dyebath brings about the coupling reaction within the fibre. Even today, azoic dyes still make a significant contribution to the dyeing and printing of cellulose.

### **Diazotisation and the aftertreatment of direct dyes**

Although direct dyes are relatively easy to apply, their fastness properties often leave room for improvement. Various treatments have been used that are based either on enlarging the dye molecules or on making them insoluble once they are in the fibre. Discussion of these processes is relevant here because these treatments may involve either diazotising a primary aromatic amino group of the dye molecule, which can then react with a coupler, or allowing the direct dye to react with a diazonium salt, so that the dye itself becomes a coupling agent. The accompanying increase in molecular size improves the fastness to wet treatments, but is often accompanied by a change in colour and a deterioration in fastness to light.

The molecules of the diazotised and developed direct dyes are so large that any attempt to apply them directly in this form would involve difficulties of penetration and levelling. Enlarging the dye molecule in this way thus expands the possibilities for the production of deep black, brown and blue dyeings.

Diazonium compounds are also sensitive to photochemical degradation. This property can be exploited in the production of photographic textile prints, by a technique similar to that used with solubilised vat dyes described on page 104. This possibility was first demonstrated by Professor Green at Leeds University, who dyed a fabric with primuline, a yellow dye, and then converted an



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amino group in the molecule to a diazonium group. The fabric was then covered with a photographic negative and exposed to light. The diazonium compound in the dyed fabric was selectively destroyed in those areas where the intensity of the light reaching the fabric was highest. Aftertreatment with a coupler thus produced a printed image with tonal gradation.

### Coloration of synthetic fibres

#### Disperse dyes

When cellulose secondary acetate and cellulose triacetate fibres were first produced in the late 1920s, they presented a serious problem to the dyer. Unlike all other known fibres of the time they were hydrophobic; since they could not be penetrated by water, they could not be dyed by water-soluble dyes. This threatened to limit the uses of the fibres, but the problem was eventually overcome by developing a new class of dye. The dyes concerned were nonionic and therefore, at the most, sparingly soluble in water. There was little point in treating the fibres with a mixture of the pure dye and water because the particles would not be distributed uniformly. Incorporating a surface-active agent with the dye powder ensures a uniform distribution of dye in the dyebath, allowing uniform dyeings to be obtained. The dye particles are thus held in dispersion by the surface-active agent and the dyes themselves are called *disperse dyes*. They are now the main class of dye for certain synthetic fibres.

#### *Nature of disperse dyes*

The main difference between the water-soluble dyes discussed previously and disperse dyes is that the latter do not contain the chemical groups (such as  $-\text{SO}_3\text{Na}$  or  $-\text{COONa}$ ) commonly incorporated to confer water solubility. Consequently disperse dyes are nonionic and as such are insoluble or only sparingly soluble in water, even at high temperatures. These hydrophobic dyes, however, are capable of 'dissolving' in the hydrophobic fibres; that is, the fibre acts like an organic solvent, extracting the dye from water. This is analogous to the simple solvent extraction of organic compounds from water by shaking up the aqueous phase with an appropriate water-immiscible solvent.

The inclusion of surface-active agents (page 31) in the dyebath is a crucial factor in the application of disperse dyes. The surface-active agents used with these dyes are usually anionic in



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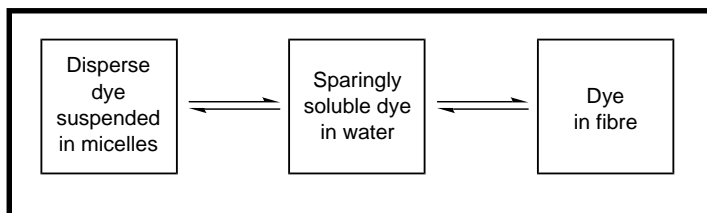


nature. Once such a compound is added to water, its dual character results in the formation of micelles above a critical, but low, concentration. The hydrophobic 'tails' of the surface-active agent molecules are inside the micelle which, as a consequence, is able to solubilise the disperse dye molecules, so conferring a higher apparent solubility on the dye. The micelles, which thus carry negative charges on their surfaces, repel each other and consequently do not coalesce. The hydrophobic chains are also adsorbed on the surface of the solid dye particles, thus further stabilising the suspension. When used in this way the surface-active agents are referred to as *dispersing agents*.

The sublimation of disperse dyes at high temperatures gave problems with the early dyes (page 18), but such difficulties can now be avoided by careful dye selection. Indeed, the sublimation properties have been exploited in the development of novel methods that permit dyeing or printing through the vapour phase.

### ***Application of disperse dyes***

Disperse dyes can be applied to most synthetic fibres using simple immersion techniques. The dye transfers to the fibre from the micelles. As micelles empty their dye, they re-form and dissolve more dye from the solid particles (Figure 5.4).



**Figure 5.4** Diagrammatic representation of the disperse dyeing mechanism

Differences in dyeing properties between one fibre type and another are accommodated by changes in the dyeing temperature. Since neither ionic attachments nor covalent linkages are formed, the dyeing process is controlled through either accelerating dyeing by raising the temperature, or slowing it down by using a higher concentration of dispersing agent. The latter expedient assists levelling of the dye in the fibre and prevents the build-up of dye particles on the surface of the filament, a fault which that otherwise leads to poor rubbing and wet fastness.

Disperse dyes can be applied to cellulose secondary acetate readily over approximately 1 hour at 80 °C. Higher temperatures are avoided as otherwise acetate groups on the cellulosic fibre can be hydrolysed to hydroxyl groups, which can spoil the surface of the fibres and reduce their

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substantivity towards the disperse dyes. Cellulose acetate fabrics are best dyed in open widths (that is, with the weft threads fully extended) to prevent the formation of creases, which show up as darker markings.

Cellulose triacetate is more difficult to penetrate with disperse dyes because of its more compact molecular structure, but it can be dyed at the boil.

Nylon fibres can be dyed under conditions similar to those used for cellulose acetate fibres. Polyester fibres and acrylic fibres present more difficulty. The closely packed polymer chains of polyester and the presence of anionic groups such as  $\text{—SO}_3\text{H}$  and  $\text{—COOH}$  in acrylic fibres permit only pale shades to be obtained under normal conditions with disperse dyes.

One widely used way of overcoming the problem with polyester is to dye at temperatures above  $100\text{ }^\circ\text{C}$ , using pressurised vessels. Temperatures as high as  $140\text{ }^\circ\text{C}$  are attained in this way. At these temperatures the molecular structure of polyester becomes more flexible, allowing faster diffusion of dye into the fibre. (Unfortunately this approach is unsuitable for acrylic fibres because at these higher temperatures destructive changes take place in the molecular structure, imparting an unacceptably harsh handle to the fabric. Very often, therefore, acrylic fibres are dyed with basic dyes, as described on page 111.)

Instead of inducing polyester fibres to take up disperse dyes by the use of high temperatures, special dyebath additives called *carriers* may be used. Their effect on the polymer chains is similar to that of a raised temperature, allowing more rapid ingress of dye and the development of deep shades. Their smell is objectionable, however, and unless they are removed completely from the fibre they can damage the light fastness of the dyeing.

There is a correlation between the dyeing behaviour of disperse dyes and fastness to heat treatments that allows the dyes to be conveniently grouped into five main application groups: A, B, C, D and 'undesignated', based on their performance with polyester. The undesignated dyes are unsuitable for use with polyester, but can be used for dyeing cellulose secondary acetate, triacetate and nylon.

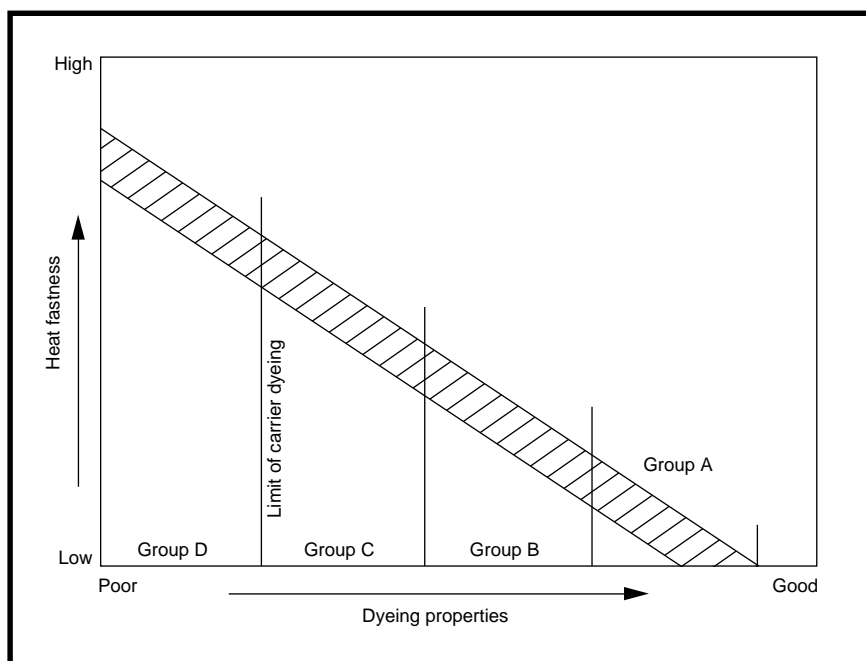
Class A dyes are suited to acetate, triacetate and nylon but are of limited value in dyeing polyester, giving poor fastness to heat. Class B dyes are excellent for use with polyester, particularly in covering variations in dyeing properties associated with textured yarns. Their fastness to heat is moderate, and some of them may be used for acetate, triacetate and nylon. Class C dyes have all-round suitability for polyester in all dyeing methods. Their fastness to heat is not the best possible,



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**Figure 5.5** The relationship between heat fastness and dyeing properties of disperse dyes; all disperse dyes have properties that place them within the shaded area on the diagram

but all can be used with acetate and triacetate. Dyes of class D are used for polyester when maximum heat fastness is required. They are unsuitable for carrier dyeing and high-temperature methods or when a pad-dry-heat process is required. Thus, as a general rule, the dyeing properties of disperse dyes become more difficult to deal with as the fastness to heat treatments increases (Figure 5.5).

Sometimes attaining a particular fastness target can present major difficulties. For example, motor car upholstery may be exposed to extreme conditions of light and heat: in tropical countries it is not unusual for the seat covers in enclosed vehicles to reach temperatures of around 100 °C. These conditions can lead to weakening and severe fading of the fabric. The manufacturers therefore require a very high standard of fastness to light. Ratings of 6–7 on the blue light fastness scale are demanded, as compared with that of 4–5 usually associated with the demands of the domestic market. Dye selection must therefore take into account both light fastness and the likely effects of the dye on the stability of the fabric. Polyesters are widely used for these covers, so the high standards have to be achieved using disperse dyes. Intensive effort has been directed towards solving this problem so that suitable dyes can be selected with confidence.

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### **Water-soluble dyes for synthetic fibres**

Acrylics and nylon, being synthetic fibres, may be dyed with disperse dyes, but they also have sufficient hydrophilic character to permit entry of some water-soluble dyes. Consequently it is possible to find acrylic fibres dyed with basic dyes and nylon fibres dyed with acid dyes.

### ***Basic dyes for acrylic fibres***

Basic dyes are only occasionally employed for dyeing silk and wool, because they have poor light fastness on these substrates. As a class, however, their light fastness on acrylic fibres is very good.

Some basic dyes have been specially prepared for acrylic fibres, and whereas most water-soluble dyes are anionic in nature (negatively charged), basic dyes are cationic (positively charged) and are held on to the fibre by the formation of salt links with anionic groups deliberately built into the fibre to provide dye sites.

Rapid heating at around 60–70 °C is to be avoided because at this temperature the dye diffuses rapidly; since the dyes are highly substantive this can lead to unlevel dyeing if the control is inadequate. In fact the initial rapid adsorption of dye is controlled by adjustment of the dyebath pH and the use of colourless cationic *retarders* which compete for dye sites.

### ***Acid dyes for nylon***

Like wool, nylon contains amino groups which under acidic conditions become acid dye sites. Consequently certain levelling acid dyes have proved suitable for use with nylon. Nylon contains many fewer amino groups than does wool, however, and there is thus a limit to the amount of dye that can become attached to the nylon fibre. When this limit is reached, or as the dye molecules become larger, hydrogen bonding to amide groups (—CONH—) becomes significant.

Diffusion of acid dyes into nylon is slower than it is into wool, and the limited number of sites can cause problems in deep mixture shades where individual dyes compete for available sites. Under these conditions the faster-diffusing dyes may block entry of a second component.



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### **Further reading**

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