CHAPTER 12

Auxiliaries associated with main dye classes

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12.1 INTRODUCTION

The aim in this chapter is to summarise the properties of auxiliaries normally used with each of the main dye classes. Where these agents have been dealt with earlier, the emphasis here is on application behaviour. Chemical details are included, however, for those auxiliaries that have not yet been mentioned; emphasis is given to the auxiliaries used rather than to processing details.

12.2 ACID DYES

Only the products associated with acid and premetallised dyes are dealt with in this section. The auxiliaries used with mordant dyes are covered in section 5.8. Anionic acid dyes, applied principally to wool and nylon, vary widely in their fastness and level-dyeing properties (section 3.2.2); in general, the higher the wet fastness of a dye the more difficult it is to apply evenly. Hence it is not surprising that the use of auxiliaries with acid dyes is related mainly to level-dyeing properties. There are two basic aspects:

1. controlling the pH to give a satisfactory dyeing rate and ultimate exhaustion
2. using auxiliaries to give additional levelling, either through a competitive mechanism that exerts further control on absorption or through the promotion of migration and diffusion.

Temperature provides another means of control although this is rarely the only technique employed. The control of pH is of particular importance, as the optimal pH varies with different types of acid dyes. This can be seen in Table 12.1, which shows the pH values generally required to give 80–85% exhaustion [1]. However, in some cases, either by modification of the dye type or by addition of certain auxiliaries, different pH values from those listed may be used.

Table 12.1 Dyebath pH values to give 80–85% exhaustion [1]

Dye class	pH
1:1 Metal-complex dyes	2.0–2.5
Levelling acid dyes	2.5–3.5
Chrome dyes	4.0–5.0
Milling acid dyes	4.5–5.5
Disulphonated 1:2 metal-complex dyes	4.5–5.5
‘Super-milling’ acid dyes	5.0–6.0
Monosulphonated 1:2 metal-complex dyes	5.0–6.0
Unsulphonated 1:2 metal-complex dyes	5.5–6.5

Levelling acid dyes and particularly 1:1 metal-complex types generally require an exceptionally low pH in order to promote exhaustion and levelling; up to 3% o.w.f. sulphuric acid is most commonly used for levelling acid dyes, although hydrochloric, formic and phosphoric acids are also effective. In the case of conventional 1:1 metal-complex dyes it is essential to use a sufficient excess of acid over and above the typical 4% o.w.f. sulphuric acid normally absorbed by the wool, otherwise there may be a tendency towards tippy dyeings and lower wet fastness. The actual excess required depends on applied depth and liquor ratio [2]; typical recommendations are given in Table 12.2.

Table 12.2 Amounts of sulphuric acid used with conventional 1:1 metal-complex dyes [2]

	Sulphuric acid (96% solution) (% o.w.f.)	
Liquor ratio	<1% dye	>1% dye
10:1	4.7	5
20:1	5.4	6
30:1	6.1	7
40:1	6.8	8
50:1	7.5	9
60:1	8.2	10

Such high concentrations of strong acid may cause fibre damage at the boil. After dyeing it is essential to ensure that the acid in the fibre is adequately neutralised. Hence formic acid (8–10% o.w.f.) is sometimes used instead, a further advantage being that it leads to less chromium in the effluent. If the dyes are modified to have one or more of the three water ligands replaced by colourless inorganic complex anions such as hexafluorosilicate $(SiF_6)^{2-}$ ligands, their dyeing behaviour is markedly altered. This facilitates dyeing at pH 3.5–4.0 with formic acid and an amphoteric auxiliary (a mixture, said to be synergistic, of quaternary and esterified fatty amine ethoxylates, polyaddition compounds of fatty amine ethoxylates and fluorosilicates) [3,4].

The use of sulphamic acid (12.1) has been recommended, resulting in a shift of pH from 1.8 to between 3.0 and 3.5 as the temperature approaches the boil, thus giving rise to less fibre damage. Typically, 6% o.w.f. sulphamic acid is added, together with an auxiliary and sodium sulphate. The change in pH arises as a result of hydrolysis of the sulphamic acid to give ammonium bisulphate (Scheme 12.1) [2,5].

$$\underset{\textit{12.1}}{NH_2SO_3H} + H_2O \longrightarrow NH_4HSO_4$$

Scheme 12.1

With the so-called 'half-milling' or intermediate levelling dyes, values in the range 1.8–3.5 would lead to too rapid a rate of exhaustion with consequent risk of unlevel dyeing. For these dyes, the optimal pH is 4.0–5.5, generally achieved using up to 2% o.w.f. acetic acid. Milling acid dyes and 1:2 metal-complex types are highly responsive to acid. Hence the tendency with these dyes is to use a pH-shift system (section 10.1), starting from neutral or slightly alkaline conditions and progressively decreasing the pH to the required level as dyeing proceeds. A hydrolysable organic ester or a latent-acid salt, such as ammonium sulphate or ammonium acetate, may be used, often with ammonia to give a higher initial pH. Whilst such techniques do not damage nylon, initially alkaline conditions can lead to some degradation of wool. Hence for wool it is preferable to choose dyes showing low substantivity at pH 7–8 but exhausting well at pH values of 6.2 or lower [2].

Figure 12.1 shows the ease with which wool is damaged in highly acidic, neutral or alkaline dyebaths [3,4]. The least damage occurs at pH 3.5–4.0, slightly lower than the isoelectric point of pH 4.5–5.0 (section 3.2.2). These considerations have led to the development of processes by which milling dyes and 1:2 metal complexes can be applied at pH values close to the isoelectric range. An effective surfactant-type levelling or retarding agent must then be used to counteract the high rate of exhaustion promoted by this degree of acidity [1–4,6–10].

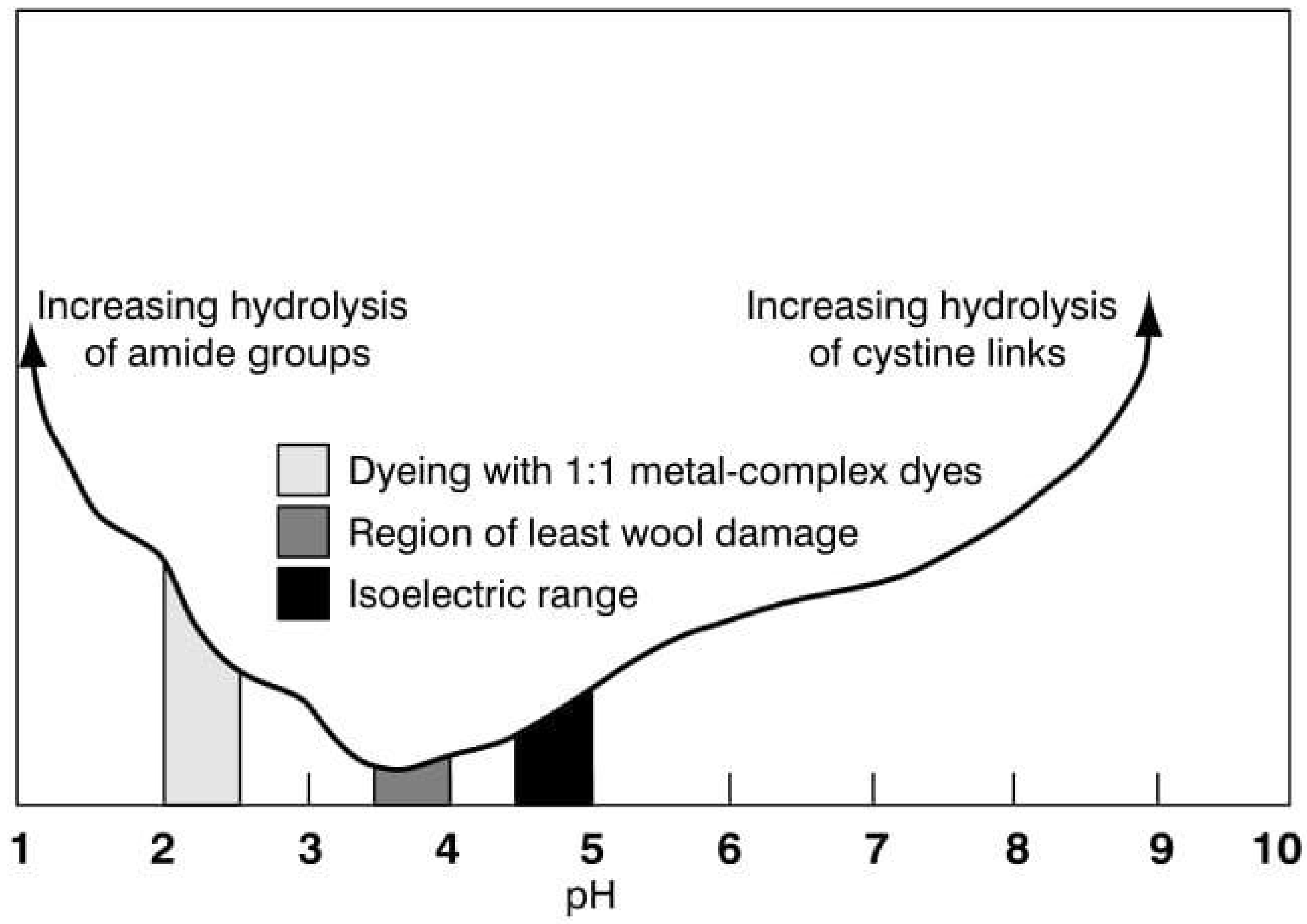


Figure 12.1 Wool hydrolysis and region of least damage as a function of dyebath pH at the boil [3,4]

In general, rather less acidity is required on nylon than on wool for application of the same combination of dyes. However, there has been some discussion regarding the best means of controlling pH [11]. In some cases, starting at pH 7 or higher with ammonium sulphate or acetate can lead to variations in pH at the end of the process, with consequential variations in performance. Better end-point control is achieved by starting at pH 6.0–6.5 using a sodium dihydrogen phosphate/disodium hydrogen phosphate buffer and ensuring a slow rise of temperature. The improved consistency of dyeing may offset the higher cost of the phosphate buffer. In some regions, however, the use of phosphates is regarded as environmentally sensitive.

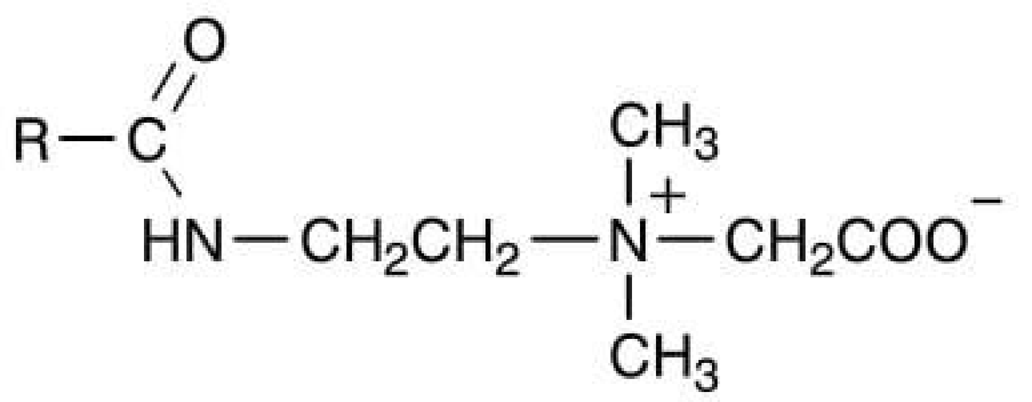
A neutral electrolyte, usually 10–20% o.w.f. sodium sulphate or sodium chloride, is often added with acid dyes to aid levelling. This action results from the competition for the dyeing sites in the fibre provided by this high concentration of inorganic anions. Ultimately these are replaced by the dye anions as a result of their higher affinity. Electrolytes are less effective as levelling agents in near-neutral dyebaths, however, since under these conditions the cationic charge on the fibre is too low to attract simple inorganic anions and dye sorption is generally through nonpolar rather than electrostatic forces. Nevertheless, it is still common to add an electrolyte when applying these dyes, although it functions primarily to boost exhaustion through a common-ion mechanism rather than as a levelling agent.

The use of surfactant-type levelling agents is of importance with acid dyes on wool and nylon, especially with dyes of relatively high wet fastness. Anionic surfactants act by competing for the cationic sites and are mainly used to counteract fibre-oriented unlevelness due to physical and chemical irregularities in the fibre. Strongly cationic quaternary compounds readily form complexes with acid dyes, but may precipitate them if used alone. Weakly cationic ethoxylated tertiary amines do not suffer from this disadvantage and are of great importance in minimising unlevelness associated with rapid dye uptake. Combinations of anionic and weakly cationic types, carefully chosen according to the principles described in section 10.7, are of particular importance since they counteract both types of unlevelness. An incompatible combination of dyes is one that does not build up on tone because of the sequential sorption of individual components. A well-chosen levelling agent, or a combination of suitable agents, can effectively convert such a mixture into a compatible one.

Amphoteric levelling agents, combining the properties of anionic and weakly cationic agents in the same molecule, have attained increasing importance [6–10]. Originally developed for the application of reactive dyes on wool, amphoteric agents have been exploited with acid dyes, particularly for dyeing at pH 4–5. They are especially suitable for the ranges of 1:2 metal-complex dyes containing ionic solubilising groups (carboxyl or sulpho) rather than the nonionised but polar groups (such as sulphonamide or sulphone) in traditional dyes (sections 3.2.2 and 5.1). These are often cheaper to manufacture and offer better wet fastness; their development and exploitation owed much to the use of amphoteric betaine levelling agents [12,13]. Although the behaviour of amphoteric agents has been studied with metal-complex and acid dyes on both wool and nylon, their main focus of interest has remained the application of reactive dyes to wool. For this reason, therefore, their application and mechanism of action are considered in more detail in section 12.7.2. Suffice to say here that the mechanisms observed are generally applicable to both reactive and acid dyes, including metal-complex types.

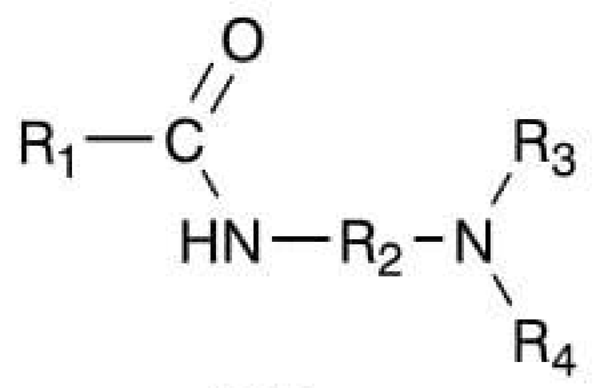
By using more than the optimal amount of dye-complexing agent required for effective levelling, some of these products can be used as stripping aids either alone for partial non-destructive stripping or in combination with oxidising agents (such as sodium dichromate and sulphuric acid) or reducing agents (such as sodium formaldehyde-sulphoxylate or sodium dithionite) for more drastic destructive stripping.

There has been long-standing interest in the so-called low-temperature dyeing of wool and, to some extent, of nylon. Generally this implies dyeing at 60–90 °C, most commonly at 80–85 °C, rather than at the traditional boil. This approach results in energy savings with both fibre types but is particularly attractive to wool dyers because it results in less damage to the fibre than when dyeing at the boil. Although some earlier methods involved the use of solvents such as benzyl alcohol or chlorinated hydrocarbons, now unacceptable on environmental, health and safety grounds, methods involving surfactants continue to generate interest, even though this does not result in widespread commercial use. Nonionic surfactants have been favoured [2,13], including ethoxylated alcohols, ethoxylated nonylphenol [2] and polyglycol esters and ethers [14]. Amphoteric auxiliaries have also given effective results. On nylon dyed at 75 °C with acid dyes, the best results were obtained [15] with the lauryl-substituted member of the fatty acylamidoethyl-*N*,*N*-dimethylglycine betaine series indicated in structure 12.2. Compounds of general formula 12.3 have been found effective with acid dyes on wool [16].



12.2

R = lauric $CH_3(CH_2)_{10}$ or palmitic $CH_3(CH_2)_{14}$



12.3

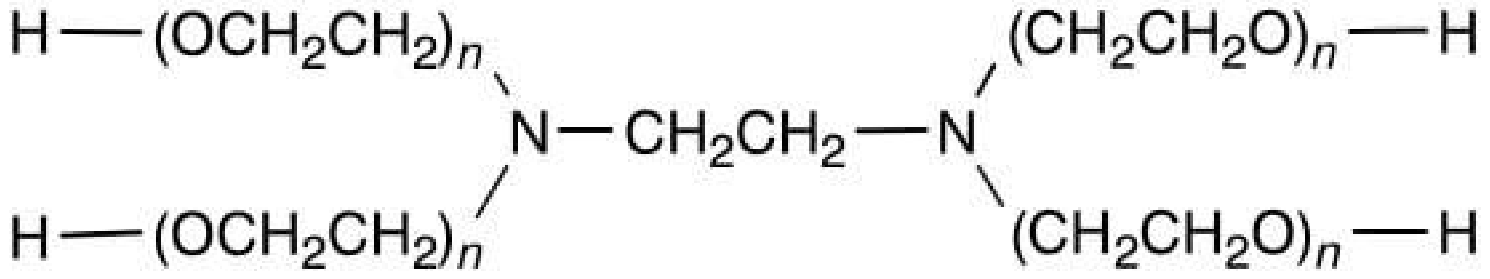
R_1 = long-chain alkyl
R_2 = short-chain alkylene
R_3, R_4 = short-chain alkyl

The most effective auxiliaries for low-temperature dyeing processes are generally those that result in accumulation at the fibre surface of an auxiliary-rich phase of high dye concentration. This implies the formation of an auxiliary-dye complex at a concentration as close as possible to the critical micelle concentration and hence usually close to the limit of solubility for the system. This complex then migrates into the fibre; depending on the applied depth, dyeing time may need to be extended. In order to meet these criteria, the nonionic types selected should have a low degree of ethoxylation, typically 4–10 ethylene oxide units per molecule. This can lead to a high degree of auxiliary-dye specificity with consequent implications for the compatibility of dyes in mixtures, as well as possible problems of precipitation as a result of low cloud point phenomena. In spite of the potential attractions, such low-temperature dyeing methods have attained only limited commercial use.

It is interesting to note that products effective in the low-temperature dyeing of wool and nylon tend to be effective in overcoming dyeability variations attributable to fibre irregularities, such as tippy or skittery dyeing in wool and barry dyeing in nylon. The amphoteric agents have proved to be particularly efficaceous in this respect, playing an important part in facilitating level dyeing with sulphonated 1:2 metal-complex dyes, which are otherwise rather prone to tippy or skittery dyeing. The phenomenon of barriness in nylon fabric dyeing has been reviewed [17,18] and the factors discussed in section 10.7 in regard to the action of levelling agents are pertinent here. Mixtures of auxiliaries are particularly effective, such as a sulphonated anionic with a fibre-substantive cationic type based on an aliphatic amine [18]. Care should be taken that such mixtures are compatible, either through the use of ethoxylated components and/or the addition of a solubilising ethoxylated nonionic agent.

In a study of ethoxylated ethylenediamine derivatives (12.4) in the application of acid dyes to nylon, covering a range of ethoxylation from 40 to 180 units per molecule (average

n = 10–45), the best initial restraining effect together with the highest uptake of dye at equilibrium was obtained with 180 ethylene oxide units (average n = 45) [19]. This highly ethoxylated ethylenediamine was found to increase dye uptake when incorporated into nylon 6 granules as an antistatic agent [20].



12.4

$$\mathrm{[H-(OCH_2CH_2)_n]_2N-CH_2CH_2-N[(CH_2CH_2O)_n-H]_2}$$

The use of liposomes as complexing agents in the application of premetallised acid dyes to wool has been investigated [21–24]. Liposomes are lipid structures containing aqueous compartments surrounded by bilayer membranes. However, the methods as yet available for the preparation of these agents are hardly practical in dyehouse terms (section 10.3.4).

It is possible to increase colour yields on wool by the use of protease or hydrolase enzymes (section 10.4.2). Although some improvement in yield was observed at temperatures as low as 50 °C, the increase was insufficient to be of commercial interest, but yields with enzyme at 85 °C were close to those obtained without enzyme at 100 °C [25].

The presence in dyehouse effluents of typical dye-complexing metal ions is an environmentally sensitive issue, such metallic contamination arising mostly from the decomposition of metal-complex dyes [26]. The synthetic complexing agent cucurbituril (section 10.3.2) can be used to selectively extract such metal ions from the effluent.

Continuous dyeing with acid dyes is most frequently carried out on loose fibre, tow or slubbing before yarn manufacture. Resilient fibres such as wool can cause problems at the immersion stage and during subsequent steaming, leading to unlevel results characterised chiefly by tippy or frosty effects. Similar effects can be observed with pile fabrics such as carpets owing to differing degrees of penetration of the pile. These defects are usually overcome using a hydrotropic agent such as urea with surfactant auxiliaries [9,12,27,28]. Certain anionic surfactants are claimed to be effective, particularly sodium dioctylsulphosuccinate and its 2-ethylhexyl and 1-methylheptyl isomers [27,28]. The mechanism involves formation of an agent-dye complex that wets the fibres evenly and forms a uniform film around them. The surfactant creates a foam during steam fixation, thus assisting the uniform transport of the dye throughout the fibre; the complex subsequently breaks down and the dye is then uniformly fixed.

Detailed accounts of the printing of wool with acid dyes and metal-complex types are available [2,29]. Typical formulation details for print pastes are given in Table 12.3. A hydrotrope such as urea or thiourea is used to increase solvation of the dyes and to act as a humectant, thereby enhancing fixation. Additional solvents, such as thiodiethylene glycol (12.5) or sec-butylcarbinol (12.6), may also be added [2]. Locust bean or guar derivatives are used as thickening agents, either alone or in combination with water-soluble British gum; high solids content is preferred for fine line effects and low solids content for larger blotch prints, because of better levelling and freedom from crack marks.

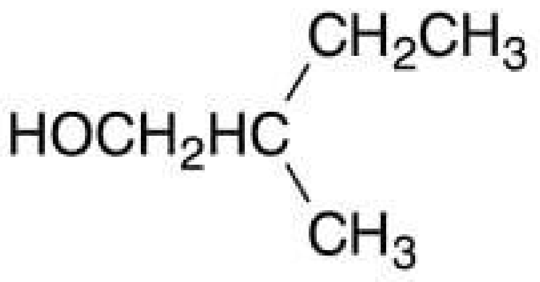
For generation of acidic conditions, a non-volatile acid such as citric acid (12.7), or an acid donor such as ammonium tartrate (12.8) or ammonium sulphate, is preferred. An acid or acid donor is not used with 1:2 metal-complex dyes of high neutral-dyeing affinity,

Table 12.3 Typical formulation for the printing of wool with acid dyes [2]

	Concentration (g/l)
Dye	*x*
Urea	50–100
Thiodiethylene glycol	50
Wetting agent	5–10
Antifoam	1–5
Acid or acid donor	10–30
Thickener (10–12%)	500
Water to give	1000

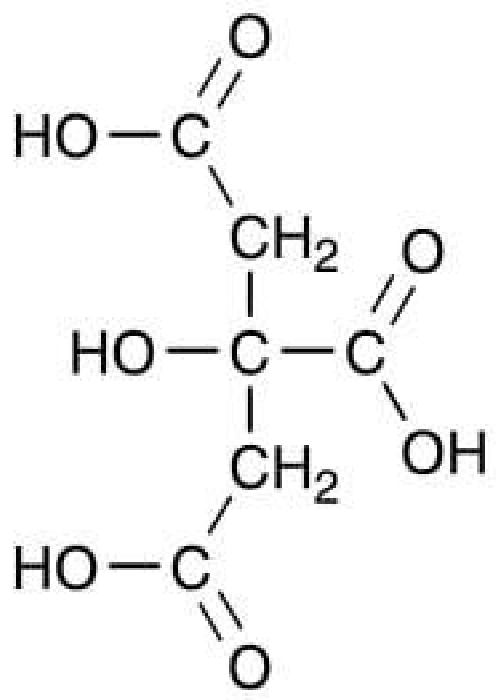
$HOCH_2CH_2SCH_2CH_2OH$

12.5

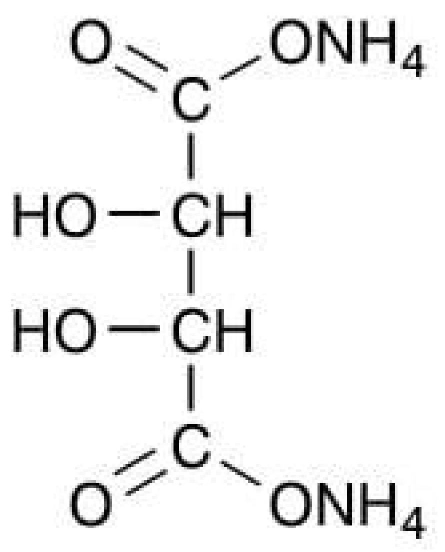


$HOCH_2HC(CH_2CH_3)(CH_3)$

12.6



12.7



12.8

however, since this may lead to destabilisation of the print paste, aggregation, specking and unlevelness. Wool or the modified natural thickeners present may tend to promote reduction of certain sensitive azo dyes; to counteract this a small amount of sodium chlorate may be added to the print paste. Defoamers and surfactants to prevent frosting may also be required.

In discharge printing a reducing agent is also required. The most widely used is zinc formaldehyde-sulphoxylate (CI Reducing Agent 6), since this functions in the weakly acidic pH range and thus gives less fibre damage. There can be problems in washing out the unsulphonated arylamines produced by reduction of certain azo dyes [2]. Sodium formaldehyde-sulphoxylate (CI Reducing Agent 2) may give excessive fibre damage since it requires an alkaline medium. The water-insoluble calcium formaldehyde-sulphoxylate (CI Reducing Agent 12) may cause screen blockage and inadequate penetration, although commercial formulation as a 30% dispersion is said to give better results. The calcium salt may be applied in admixture with the sodium salt. Thiourea dioxide is rarely chosen because of its low solubility (only 37 g/l at 20 °C) [2].

The washing-off of prints is best carried out with anionic polycondensation products of arylsulphonic acids [29] since these can improve the wet fastness of anionic dyes.

12.3 AZOIC COMPONENTS

There are three main demands for auxiliaries in the application of azoic components [30–32]:

(a) the composition of the naphtholate solution
(b) the composition of the diazo solution (developing bath)
(c) aftertreatments to develop hue and maximum fastness.

These will be considered first in relation to batchwise application, followed by variations pertinent to continuous dyeing and printing. The discussion relates solely to cotton, by far the most important substrate for these dyes; application to other cellulosic substrates follows generally similar principles, the main difference being in product concentrations.

12.3.1 Composition of the naphtholate solution

A primary requirement for naphtholate preparation is soft water; otherwise, insoluble calcium or magnesium naphtholates will be formed. If soft water is not available then a sequestering agent must be added, the sodium hexametaphosphate, EDTA or NTA types (section 10.2) being suitable. A little alcohol is generally added during the initial pasting and dissolving of the naphthol. Given water of suitable quality, the naphtholate bath in batchwise dyeing then usually contains the following additions:

- alkali, most often sodium hydroxide, although in certain circumstances (particularly with regenerated cellulosic or bast fibres) sodium carbonate or trisodium orthophosphate may be used [31]
- a protective colloid (dispersing agent) and perhaps a wetting agent
- formaldehyde
- electrolyte, either sodium chloride or sodium sulphate.

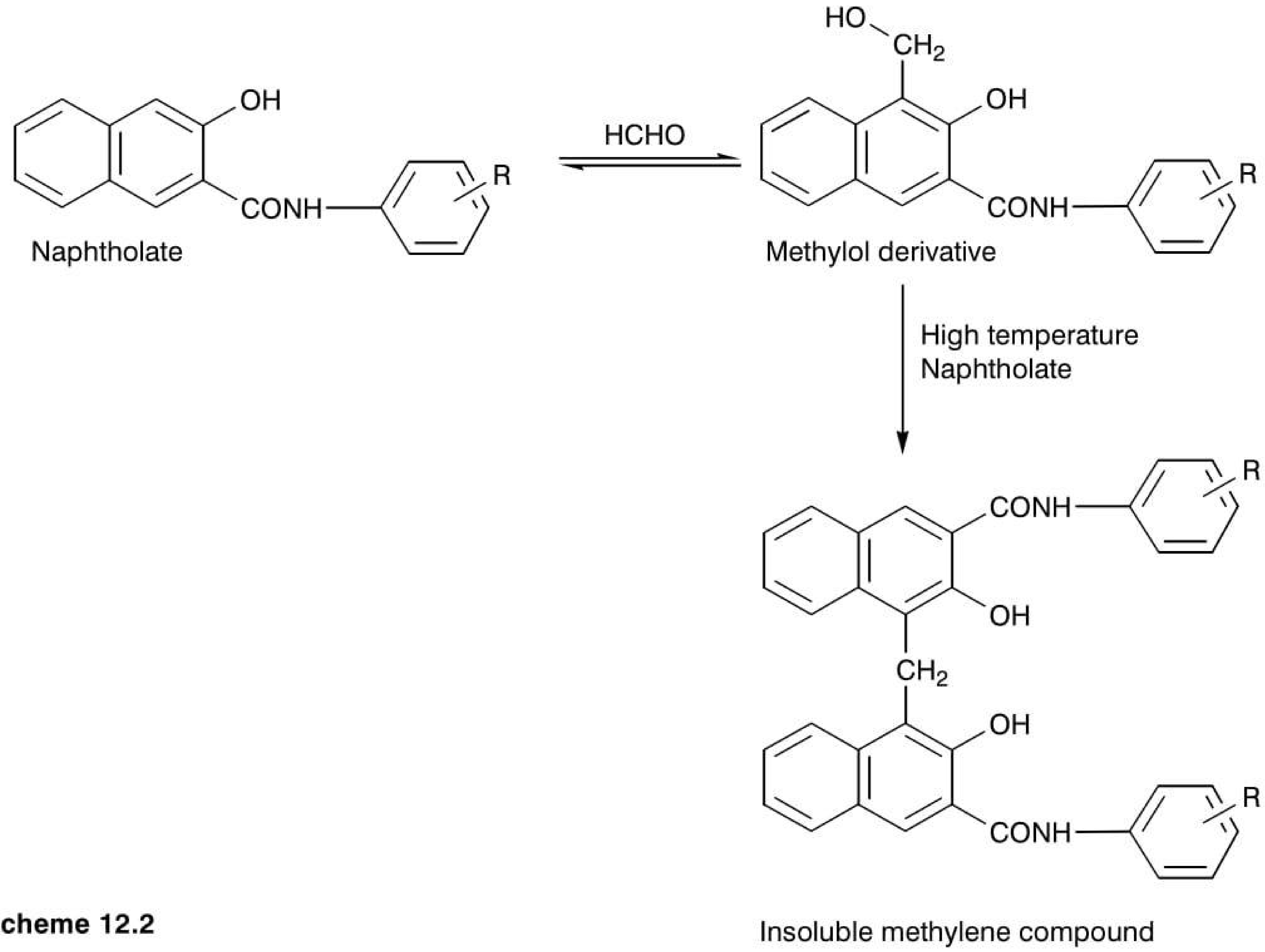
The purpose of the alkali is to convert the insoluble free naphthol into its colloidally soluble sodium salt. An excess of sodium hydroxide is generally needed but too much will tend to promote hydrolysis of the amide groups present in most azoic coupling components. The actual amount required varies with the naphthol and processing conditions; the manufacturer's detailed literature must be consulted.

The protective colloid/wetting agent may be a single anionic agent; Turkey Red Oil, for example, combines both functions but is prone to form a precipitate in hard water. Only anionic types are suitable, since nonionic and cationic types generally cause precipitation [31]. Most protective colloids are of the following types:

(a) lignosulphonates
(b) protein-fatty acid condensates
(c) sulphonated condensates of aromatic compounds, especially of phenols and naphthols with formaldehyde.

The chemistry of these product types has been described previously (section 10.6.1). The anionic polyelectrolyte helps to stabilise the colloidal solution of the naphtholate, through a mechanism similar to that already described. Where the protective colloid itself does not give adequate wetting of the fabric a suitable wetting agent, which in batchwise dyeing must function well in the cold, should be added; the alkylnaphthalenesulphonate types are suitable.

The formaldehyde plays an important role in counteracting the tendency of amide-containing naphtholates to hydrolyse at high pH values to the *o*-carboxynaphthol, which couples to give coloured by-products of inferior fastness. Its protective action is in addition to that provided by the excess alkali and its use is recommended with most naphthols, exceptions being yellow acetoacetarylamides where coupling is inhibited. Formaldehyde operates through the reversible formation of a 1-methylol derivative at 40–50 °C, but at temperatures above 50 °C this derivative reacts with a second molecule of naphtholate to give a non-coupling dinaphthylmethane compound (Scheme 12.2) [30].



Scheme 12.2

The naphthols used in batchwise dyeing are moderately substantive and their exhaustion is improved by electrolyte addition, with consequent improvement in yield and fastness properties. The amount of electrolyte required varies with the substantivity of the naphthol, the depth applied, liquor ratio and substrate quality, but generally ranges from 10 to 40 g/l sodium chloride or sodium sulphate. Higher amounts are required for heavier depths of low-substantivity naphthols in long liquors. With high-substantivity naphthols on substrates that are difficult to penetrate and short liquor ratios, treatment is begun in a salt-free naphtholate solution and electrolyte is added later. After application of naphthols by batchwise techniques, excess surface naphthol is usually minimised or removed by hydroextraction, suction, squeezing or by rinsing in 10–50 g/l electrolyte and 0.3–0.6 g/l sodium hydroxide solution.

Batchwise application of naphthols is generally carried out at 20–30 °C. Although a higher temperature may be chosen to improve the penetration of difficult substrates, it should not be allowed to rise above 50 °C; substantivity decreases with increasing temperature. In continuous dyeing, however, in order to ensure uniformity of uptake from the pad bath, the requirement is for minimal substantivity. Hence application temperatures are generally high (80–95 °C) and naphthols of low to medium inherent substantivity are used. These factors indicate a need for the following modifications to the auxiliary formulations used:

(a) formaldehyde should be omitted due to formation of the non-coupling dinaphthylmethane derivative at temperatures higher than 50 °C
(b) electrolyte should be omitted
(c) the amount of wetting agent can be reduced, or it may be omitted if the higher temperature together with the protective colloid provide sufficient wetting.

Naphtholates in the form of ready-to-use solutions are now available [31,32]. These are formulated to contain the essential auxiliaries, are quite stable on storage and offer the following advantages:

- no dissolving or boiling necessary
- no dust during weighing and preparation and therefore cleaner working conditions
- shorter times for setting up the process.

12.3.2 Composition of the diazo solution or developing bath

This bath is essentially a dilute solution of a diazonium salt produced either by the diazotisation of an arylamine (Fast Colour Base) or by simply dissolving a stabilised diazonium compound (Fast Colour Salt). Soft water is desirable but not essential. General additions for batchwise dyeing with Fast Colour Bases include acid, sodium nitrite and possibly ice, together with a dispersing agent. Hydrochloric acid is the most widely used acid to effect dissolution of the base and activation of the sodium nitrite so as to bring about diazotisation. Temperatures must be kept low (5–15 °C) to avoid decomposition of the relatively unstable diazonium salt (section 4.3.1); hence ice is often added to the solution. A dispersing agent is used to ensure the fine and uniform dispersion of the azoic dye as it is formed during coupling. Only nonionic types such as fatty alcohol ethoxylates (section 9.6) are suitable, as anionic or cationic types may cause precipitation [31].

Once diazotisation is complete the excess hydrochloric acid must be neutralised before the diazonium salt is coupled with the naphthol, usually by addition of an alkali-binding agent. The agent most commonly used is sodium acetate, which by reaction with the hydrochloric acid produces acetic acid, so that the resultant mixture of acetic acid and sodium acetate acts as a buffer. The acetic acid/sodium acetate balance must be adjusted to suit specific needs related to the reactivity or coupling energy of the system (section 4.4), giving a pH varying from 4 to 5.5 for those having high coupling energy to 6–7 for those with low coupling energy. Examples of azoic diazo components and their relative coupling energies are given in Table 7.2 of reference [30]. Sometimes buffer systems utilising sodium dihydrogen phosphate and disodium hydrogen phosphate or sodium bicarbonate are preferred.

When Fast Colour Salts are used hydrochloric acid and sodium nitrite are obviously not required, although some Fast Colour Salts do need an addition of acetic or formic acid. The nonionic dispersing agent is still necessary but as most Fast Colour Salts contain an alkali-binding agent (aluminium sulphate, zinc sulphate, magnesium sulphate or, in a few cases, chromium acetate) to give the required pH, the only electrolyte additions to the developing bath are to correct any local variations in pH.

In some cases, as in the batchwise application of diazo components, it may be advisable to add electrolyte to the developing bath to inhibit bleed-off of low-substantivity naphthols. Otherwise the auxiliaries for batchwise and continuous application of diazo components are essentially the same.

Fast Colour Bases in the form of ready-to-use solutions or dispersions are now available [31,32]. As can be seen from their advantages listed below, their use has implications regarding the addition of auxiliaries:

- the formulations are resistant to freezing temperatures and stable in use
- all except one product can be diazotised without the addition of ice provided the bath temperature does not exceed 20 °C
- diazotisation is complete in 2–5 min compared with up to 30 min for conventional Fast Bases
- no nitrous gases are formed during diazotisation
- these formulations already contain a dispersing agent and no further addition is needed
- no dusting or formation of lumps as during dissolution of conventional Fast Bases.

12.3.3 Aftertreatments to develop hue and maximum fastness

After the coupling (development) process is complete the goods are rinsed, acidified and given an alkaline soaping treatment. This not only substantially removes surface dye but also brings about a process of aggregation of dye molecules within the fibre, thus developing the full potential of hue and fastness. A combination of Marseilles (olive oil) soap (3–5 g/l) with sodium carbonate (batchwise 1–2 g/l, continuous 2–3 g/l) is traditionally used. A polyphosphate sequestering agent is needed if the water is hard. A second wash with a nonionic surfactant is also required.

The conventional technique in printing is to apply the naphthol by padding as described for continuous dyeing, followed by printing with the diazo componenents using cellulose ether, locust bean or guar derivatives as thickening agents. In other respects the auxiliaries and general processing requirements are similar to those described above. A different system involves application of the naphthol coupling component and a stabilised diazonium salt in the same print paste followed by neutral steaming to effect development; a starch ether thickening agent is recommended for this process [29]. In certain resist styles aluminium sulphate is applied by printing onto naphthol-treated fabric; this brings about a localised reduction in pH that inhibits coupling during subsequent application of the diazo component, thus giving rise to a resist effect [29].

Overall, the application procedures for azoic dyeing are quite complex since many factors must be taken into account, such as:

- the specific naphthol and diazo components selected, with regard to molecular characteristics, substantivity and applied depth
- the application method, e.g. continuous or batchwise, paying attention particularly to liquor ratio and substantivity in the latter case
- the substrate, including unmercerised or mercerised cotton, causticised regenerated cellulosics or bast fibres.

All the above criteria influence the concentrations of the various components required. Some indication of how they are affected can be gleaned from reference [30]. It is important therefore to consult detailed information from the supplier of the naphthols and bases. Such information available on disc for use on a personal computer has been provided for the batchwise dyeing of cellulosic yarns [31] and the continuous dyeing of cellulosic fabrics [32].

The stripping of fully developed azoic dyeings can often be carried out using a hot solution of sodium hydroxide (1.5–3 g/l), sodium dithionite (3–5 g/l) and a surfactant; addition of anthraquinone (0.5–1 g/l) generally increases the effectiveness of the process. Yellow azoic dyeings are resistant, however, and can only be partially stripped [30]. On the other hand, stripping of naphtholated material before it has been coupled with the diazo component can be done quite effectively in boiling alkali.

12.4 BASIC DYES

There are two major characteristics of basic dyes applied by exhaustion techniques to acrylic fibres:

(1) below the glass-transition temperature (about 80 °C) exhaustion is very slight, becoming much more rapid at temperatures only a little above this
(2) very little, if any, migration occurs at temperatures up to 100 °C.

Consequently the rate of dyeing, and hence levelness, are very difficult to control; the degree of difficulty varies from fibre to fibre, generally tending to a maximum for readily dyeable fibres with a high glass-transition temperature. Owing to the sensitivity of some basic dyes to alkaline hydrolysis, these dyes vary in their response to dyebath pH, again depending on fibre type (section 3.2.4). The pH must be controlled to within 4.0 to 5.5 in order to obtain reliable, reproducible results across the range of dyes and fibres. Hence in the conventional batchwise application of basic dyes to acrylic fibres, auxiliaries must fulfil two functions:

(1) to give the required pH
(2) to control the rate of sorption in the critical temperature region and, as far as possible, to promote migration.

A buffer system is preferred for the control of pH, the most common one being the relatively cheap acetic acid/sodium acetate system, although a simple addition of acetic acid may be adequate with water that does not show a significant pH shift on heating.

The major variables are undoubtedly the rate of temperature rise and the use of retarding agents to control level dyeing. A review of acrylic fibres and their processing is available [33]; here we are concerned only with the essential chemistry of the auxiliaries used, particular emphasis being given to retarding agents.

Cationic types of retarding agent are especially important. These function essentially as colourless cationic moieties competing for the anionic sorption sites in the fibre. Quaternary ammonium compounds (section 9.5) largely predominate; their fundamental structure (12.9) offers the possibility of varying up to four substituent groups around a quaternary nitrogen atom, and hence the variety of possible structures is enormous. A range of these compounds examined for their retarding effect in the application of basic dyes [34] gives some idea of the possibilities (Table 12.4). The selection of a retarder depends on several factors, however, of which the most important are the rate and extent of sorption of the retarder compared with those of the dyes. The dyeing kinetics of basic dyes in mixtures are now universally denoted by compatibility values covering the range from 1 to 5 [35–38]. Simply varying the substituents in otherwise structurally similar dyes can change their compatibility values [37]. The sorption properties of quaternary ammonium compounds can be varied and characterised similarly, as seen from the examples shown in Table 12.5 [39], which were obtained using a titration-spectrophotometric method [40].

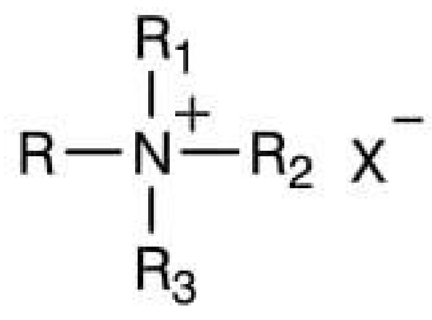
The type of associated anion has only a minor effect on the properties of a cationic retarder. General practical experience [39,41] suggests that optimal control is achieved if the

Table 12.4 Structures of some typical retarding agents [34]

Substituents in quaternary ammonium compound 12.9				
R	R_1	R_2	R_3	Anion X
$C_{12}H_{25}$ (dodecyl)	CH_3	CH_3	CH_3	Cl
Coco*	CH_3	CH_3	CH_3	Cl
$C_{16}H_{33}$ (hexadecyl)	CH_3	CH_3	CH_3	Cl
$C_{18}H_{37}$ (octadecyl)	CH_3	CH_3	CH_3	Cl
Tallow**	CH_3	CH_3	CH_3	Cl
Coco*	CH_3	CH_3	CH_3	CH_3SO_4
Coco*	CH_3	CH_3CH_2	CH_3	CH_3SO_4
Coco*	CH_3	$C_6H_5CH_2$	CH_3	Cl

* Consisted of approximately 47% C_{12} and 18% C_{14} with lesser amounts of C_8, C_{10}, C_{16} and C_{18} hydrophobes.

** Consisted of approximately 48% oleyl, 27% cetyl and 13% stearyl, with minor quantities of others.



$$R-\overset{\overset{R_1}{|}}{\underset{\underset{R_3}{|}}{N^+}}-R_2\ X^-$$

12.9

Table 12.5 Compatibility values of retarding agents [39]

Substituents in quaternary ammonium compound 12.9				Compatibility value assigned by experiment
R	R_1	R_2	R_3	
$C_{14}H_{29}$	CH_3	$C_{14}H_{29}$	CH_3	1.0
$C_6H_5CH_2$	CH_3	$C_{14}H_{29}$	CH_3	2.5
CH_3	CH_3	CH_3	$C_{14}H_{29}$	3.0
$C_6H_5CH_2$	CH_3	$C_{7-9}H_{15-19}$	CH_3	5.0
$C_6H_5CH_2$	CH_3	$C_6H_5CH_2$	CH_3	>5.0

retarder has a compatibility value equal to or slightly lower than that of the dyes, so that it will tend to be absorbed by the fibre either at the same rate as the dyes or somewhat more quickly. If the compatibility value of the retarder is significantly lower than that of the dyes, then there is a very real tendency for it to act as a blocking agent (with attendant problems), whilst if its compatibility value is much higher its efficacy is impaired.

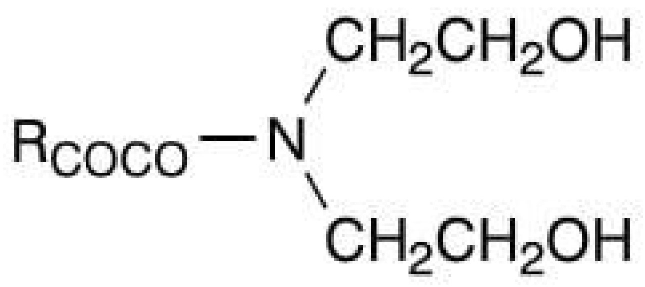
Once the substituents in the quaternary ammonium compound have been selected, consideration must be given to the applied concentration of retarder. Acrylic fibres vary significantly in the number of anionic sites available for sorption of cations but it is generally assumed that maximum likelihood of level dyeing occurs when the number of cations in the system (retarder as well as dyes) is just enough to saturate the anionic sites in the fibre. Thus the amount of retarder needed to achieve this theoretical saturation will vary from fibre to fibre, and also depends on the applied concentrations of the dyes. More retarder will be needed for fibres of high saturation value and for lower applied depths; the actual quantities required to satisfy the given conditions are generally specified by the dye manufacturers. However, the use of these theoretical quantities can lead to lower degrees of dye exhaustion within normal dyeing times. In any case level dyeing is not just simply a function of the ionic dye–fibre system but involves many other aspects, especially physical factors such as substrate form and machinery efficiency. It may well be that in a given practical situation there may be little or no level dyeing problem, so why use any more retarder than is necessary to ensure a level dyeing under practical conditions? Experience suggests that much less than the theoretical amount of retarder will often be adequate and this will help to alleviate any problems due to saturation if subsequent reprocessing for shade correction is needed.

In addition to having an effect on the rate of dyeing, cationic retarders will assist migration to an extent that depends on the fibre and the substantivity of the dyes. Retarders tend to diffuse more quickly than dyes and to be absorbed at lower temperatures (typically 65–70 °C, compared with 80–85 °C), although the magnitude of these effects will depend on the structure and properties of both retarder and dye. In some cases, such as hank dyeing on machines with poor circulation or inadequate temperature control, it may be preferable to use a retarder that almost totally restrains the uptake of dye until the top temperature has been reached, after which dye sorption takes place gradually.

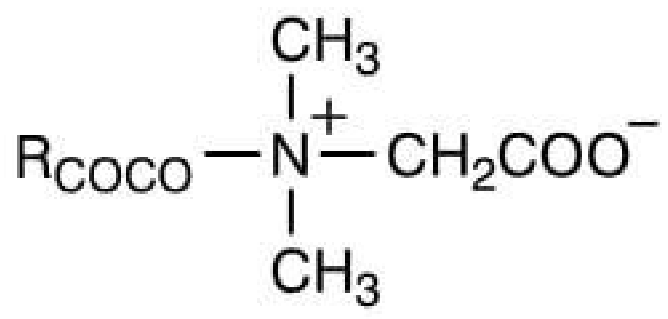
A useful general classification of cationic retarders according to their properties has been given [42]:

(a) strongly cationic with a strong blocking effect
(b) moderately cationic with a weak blocking effect
(c) weakly cationic with no blocking effect
(d) products with little or no retarding effect but giving some levelling.

Products in groups (b) and (c) allow for greater safety margins and give optimal exhaustion curves in bulk practice, although they may be more expensive than products in group (a). The main need for retarding activity arises during the critical exhaustion phase as the temperature increases from about 80 °C to the boil. Therefore some cationic retarders have been designed to hydrolyse progressively in this temperature region, so reducing the retarding activity in the later stages of dyeing and safeguarding against blocking effects. Subsequent shading and redyeing are then less problematical. Furthermore, the amounts of hydrolysing retarder used are perhaps less critical than with their non-hydrolysing

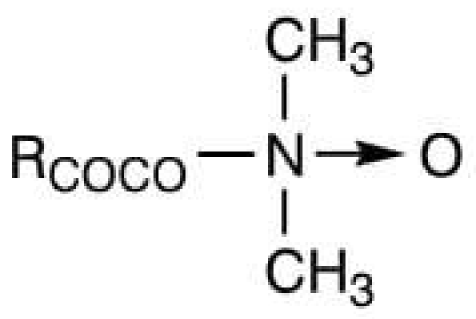


12.10



$$\mathrm{R_{COCO}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\overset{+}{\mathrm{N}}}}-\mathrm{CH_2COO^-}$$

12.11



$$\mathrm{R_{COCO}}-\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}}\rightarrow \mathrm{O}$$

12.12

counterparts, although more may be needed initially to obtain an equivalent retarding effect. A combination of hydrolysing and non-hydrolysing types may be used in some circumstances.

On 100% acrylic materials the quaternary ammonium retarders are used almost exclusively. Other types have been evaluated, however. For example, saturated alkylamines (RNH_2; $R = C_{10}$, C_{12}, C_{14} and C_{16} hydrophobes) were found to be just as effective as the quaternary types although other factors, such as aqueous solubility at the optimal dyebath pH and resistance to subsequent discoloration, favour the quaternary compounds [34]. On the other hand, bis(hydroxyethyl)cocoamine (12.10) had relatively little effect and the amphoteric carboxymethyldimethylcocoamine (12.11) none at all, although dimethylcocoamine oxide (12.12) was quite an effective retarder [34]. Other cationic compounds used [43,44] have included alkylpyridinium salts, imidazoles and imidazolinium salts, alkyldiamines, alkylpolyamines, as well as sulphonium and phosphonium derivatives.

Polymeric cationic retarders that contain up to several hundred cationic groups per molecule have been proposed [45–47]. The early types [45,46] were described as quaternised polyamines (section 9.5) of relative molecular mass 1000–20 000, as compared with 300–500 for conventional quaternary ammonium compounds. Polyacrylamides of molecular mass 2500–780 000 have been evaluated more recently [47].

These agents, because of their large molecular size, do not diffuse into the fibre but are strongly adsorbed at the fibre surface, reducing its anionic potential. They retard the dyeing rate far more than does an equal concentration of a conventional quaternary agent, but do not assist migration. Some of these products can adversely affect the compatibility of dyes as a result of selective behaviour but are said to be free from blocking effects. They do not interfere with crimp development as conventional retarders sometimes do and are particularly effective in giving superior coverage of bicomponent fibres. Since they are not absorbed into the fibre but concentrate their activity at the surface, these polymers are effective at much lower concentrations than are conventional types and this favours their cost-effectiveness. Their retarding action is sustained throughout the dyeing cycle.

Nevertheless, it does appear that the molecular mass of the polymer needs to be optimised in relation to the type of dyes used [46,47] With polyacrylamides [47] for example, a dye of small molecular size responds best to a retarder of large molecular size, and vice versa. These effects have been explained on the basis of the relative ease of diffusivity of the dyes through the polymeric retarder to reach the fibre surface. Thus a dye of small molecular size needs the extra resistance to diffusion of a retarder of great molecular mass, whilst such a retarder would present too effective a barrier to diffusion of a dye of larger molecular size. This relationship clearly has major implications for the selection of dyes to achieve close compatibility in mixture recipes. Despite the claimed advantages and the prediction as long ago as 1973 that polymeric retarders would rapidly become the preferred choice for dyeing acrylic fibres with a high content of dye sites [45], they have not attained a commercially significant role.

Retarders of opposite ionic charge to the dyes can be used [33,36,48–51]. Anionic retarders function by forming a thermally labile complex with the dye and thus lowering the substantivity of the dye for the fibre. Undesirable precipitation of this complex, which is one of the drawbacks of the system, can be inhibited:

(a) by using excess anionic agent
(b) by using an anionic agent that contains two or more sulphonate groups so that the resultant 1:1 complex retains solubility
(c) by incorporating a nonionic agent as an antiprecipitant.

Examples include sodium dinaphthylmethanesulphonates (section 10.6.1) and polyethoxylated alkylarylsulphates (section 9.4). Polymeric types, such as polystyrene sulphonate, have been tried but do not seem to offer any advantages.

The advantages and disadvantages of anionic retarders can be summarised as follows. The advantages include:

(a) the system is compatible with anionic dyes and anionic dispersing agents in the dyeing of fibre blends
(b) there is no blocking of dyeing sites in the fibre
(c) they have no adverse effects on the bulkiness of certain bicomponent fibres
(d) they promote good migration of dyes
(e) they can be used as stripping agents to reduce the depth of colour in reprocessing.

The disadvantages include:

(a) to prevent precipitation the quantity of anionic retarder should increase with increasing quantity of dye (the opposite of the situation with cationic retarders) and this conflicts with requirements for promoting exhaustion; hence exhaustion of dye when applying medium or heavy depths is poor
(b) they show less levelling during the exhaustion stage
(c) the use of cationic softeners in the dyebath is not possible.

In practical terms the disadvantages outweigh the advantages, thus limiting the importance of anionic retarders.

Electrolytes such as sodium chloride and sodium sulphate tend to retard dyeing [36,52,53] through preferential adsorption and subsequent displacement by the dye of the more mobile sodium ions, although the effect is relatively weak even compared with the weaker cationic retarders. Nevertheless, the use of up to 10% o.w.f. sodium sulphate in combination with a cationic retarder may enable the amount of the latter to be reduced by up to 20–30% [36]. The limitations of electrolytes, apart from this lower effectiveness, are that they reduce the final uptake of dye, their effectiveness decreases with increase in temperature and their effect is greatest with fibres containing weakly anionic groups such as carboxylate, rather than stronger ones such as sulphonate. Cationic softeners for acrylic fibres are sensitive to the presence of electrolytes, although sulphate-tolerant softeners may be used.

The retarding effect of electrolytes in the application of basic dyes to acrylic fibres increases with increasing concentration of salt up to a certain level. Increasing the concentration beyond this point has no further effect on exhaustion with certain univalent anions, whilst with multivalent types there is an increase in dye sorption (Figure 12.2)

[54,55]. These results have led to the conclusion that ionic mechanisms alone do not entirely explain the complex interactions that occur between basic dyes and acrylic fibres. Hydrophobic interaction also plays an important part and it has been demonstrated [55] that multivalent anions such as sulphate or phosphate can enhance the hydrophobic interaction, thereby also increasing dye sorption in some circumstances. Whilst such results are of interest in terms of dyeing theory, it is extremely doubtful whether there will ever be practical interest in exploiting the use of electrolytes at such high concentrations.

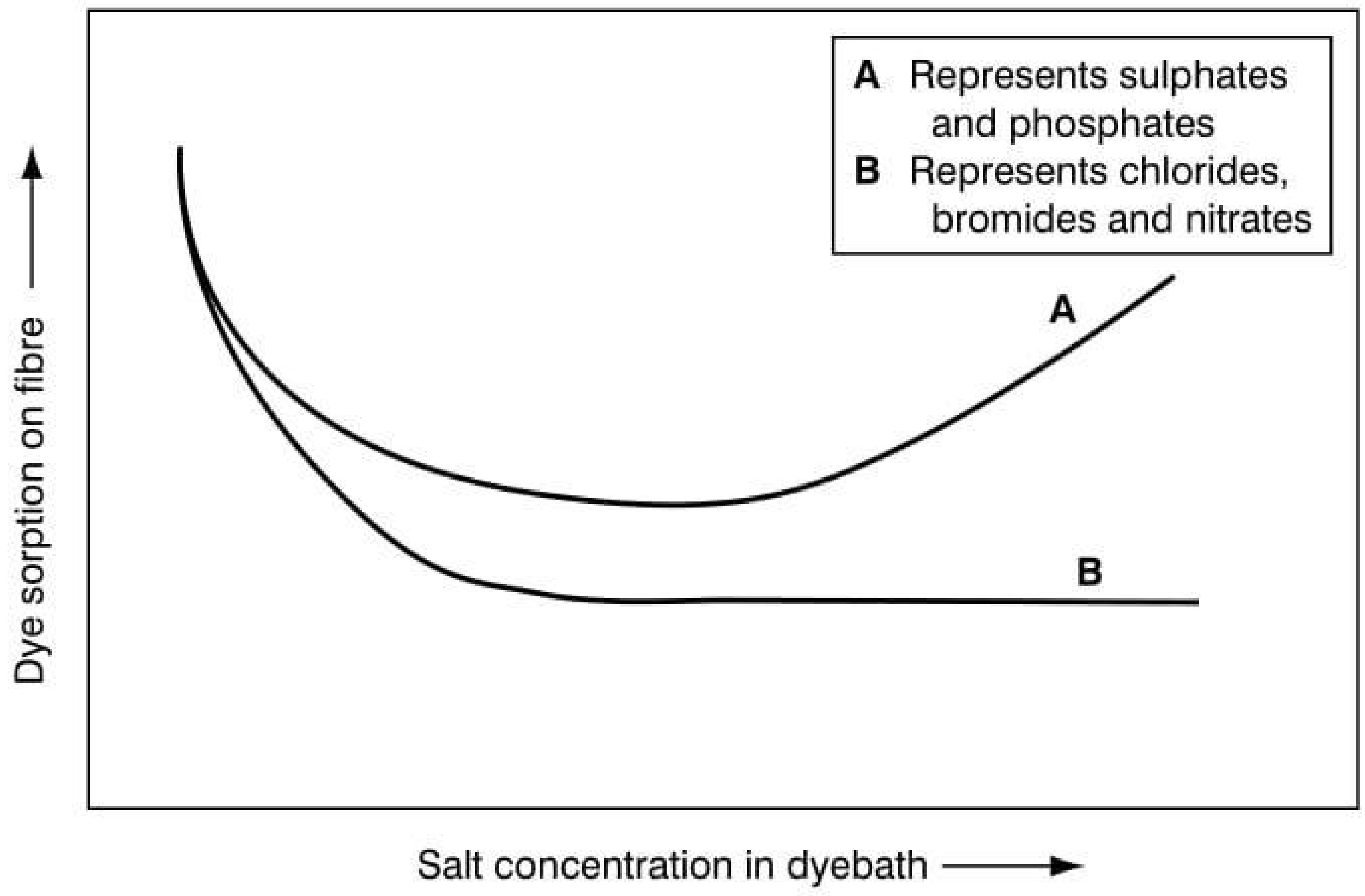


Figure 12.2 The effect of salt on the equilibrium sorption of basic dyes on acrylic fibres [54,55]

The use of dye-solubilising agents such as urea or thiourea is more usually associated with continuous dyeing or printing. However, such compounds have also been investigated for their effects in exhaust dyeing [56,57]. These compounds increase the rate of exhaustion and exert their maximal accelerating effect at low temperatures (e.g. 80 °C) and low dye concentrations. Despite the higher acceleration factor at 80 °C as compared with 100 °C, the ultimate yields at 80 °C are lower than at 100 °C (Figure 12.3) [57]. When dyeing at 100 °C or above it is difficult to see any commercial reason for making these additions, particularly in view of environmental concerns regarding such compounds.

Continuous dyeing of acrylic fibres with basic dyes [50,58,59] generally requires the use of saturated steam for fixation. As in batchwise dyeing there is a need to maintain an optimum pH of 4.5–5.0. If a sodium acetate/acetic acid buffer were to be used the acetic acid may volatilise in the steam, leading to development of alkalinity; hence it is usual to utilise a non-volatile acid such as citric acid (12.7) or tartaric acid (12.14). The thickening agent for use with basic dyes must not be anionic, a useful choice being galactomannan-based locust bean gum. Hydrotropes and fibre-swelling agents assist dye solubilisation and fixation; compounds used include thiodiethylene glycol (12.5), dicyanoethylformamide (12.15) and potassium thiocyanate (KSCN). A nonionic wetting and solubilising agent may also be useful.

In general, for the pad–steam application of basic dyes to acrylic fibres, the auxiliaries are selected to increase the solubility of the dyes with minimal retardation and maximal improvement of fixation. In a detailed statistical study along these lines [60], it was

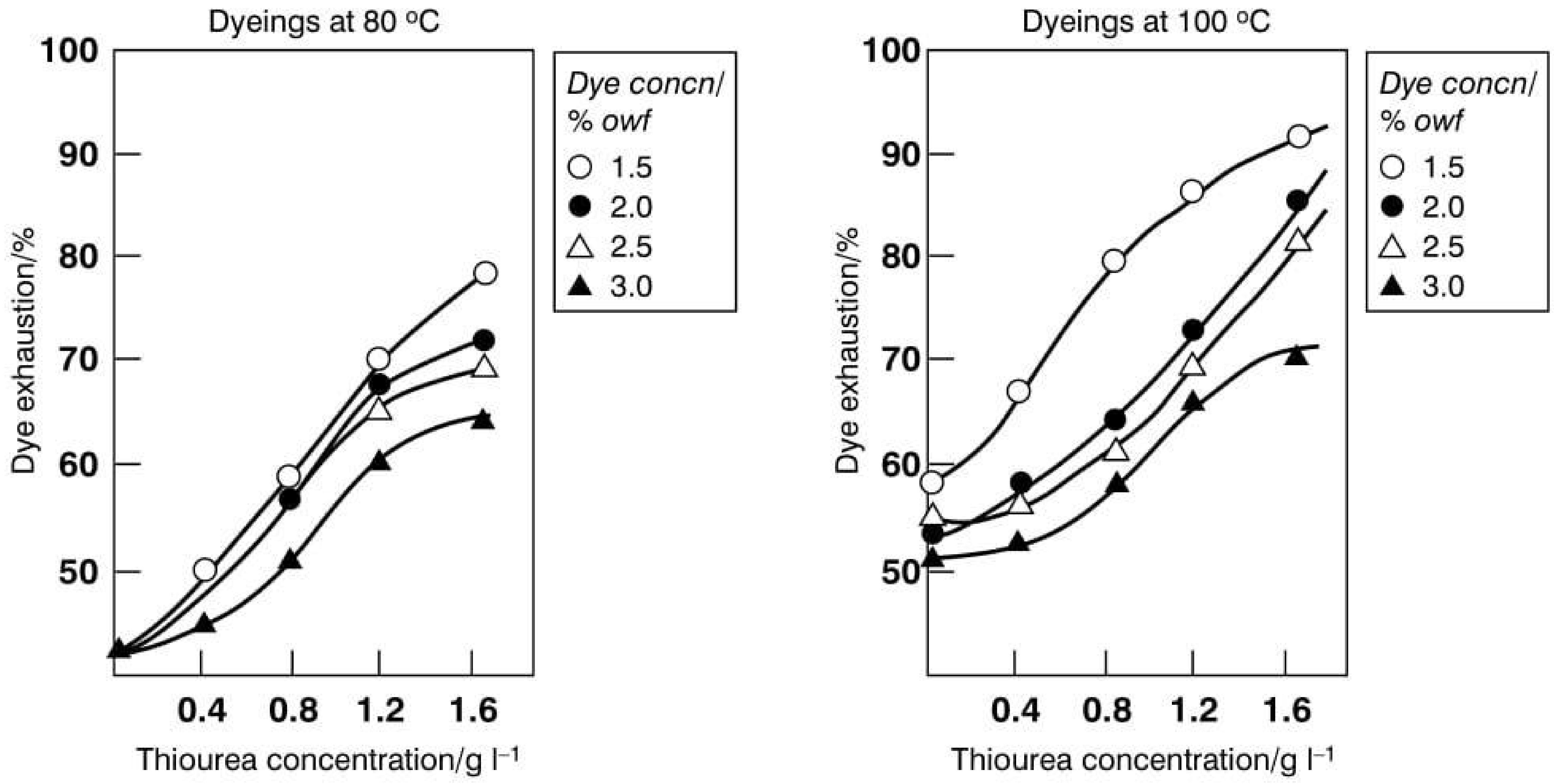
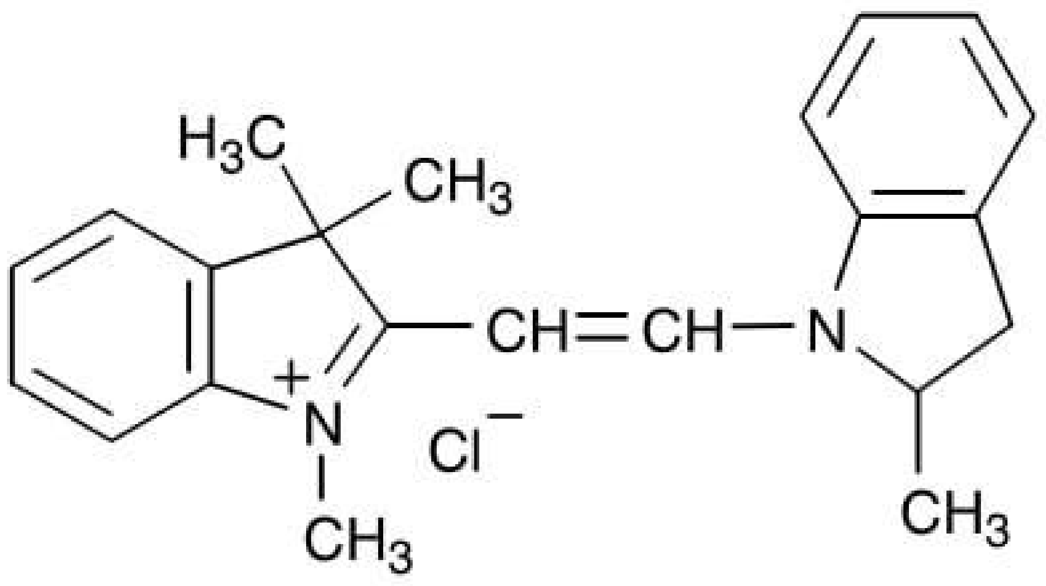
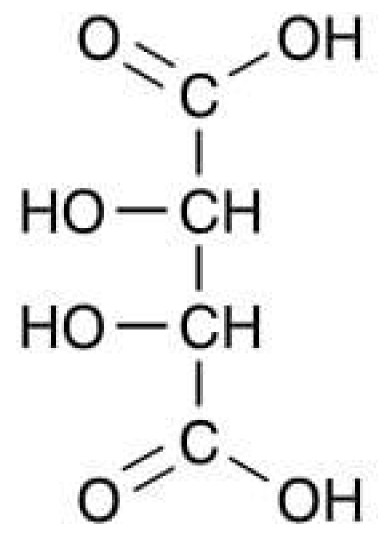


Figure 12.3 Effect of thiourea on exhaustion of CI Basic Yellow 21 (12.13) by acrylic fibres [57]

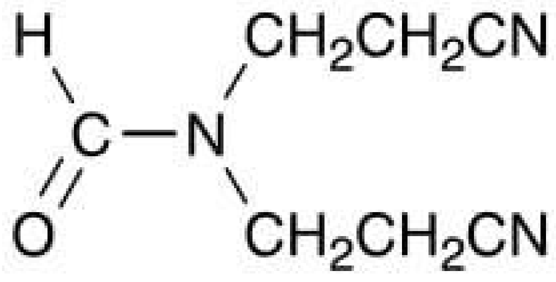


12.13

CI Basic Yellow 21



12.14



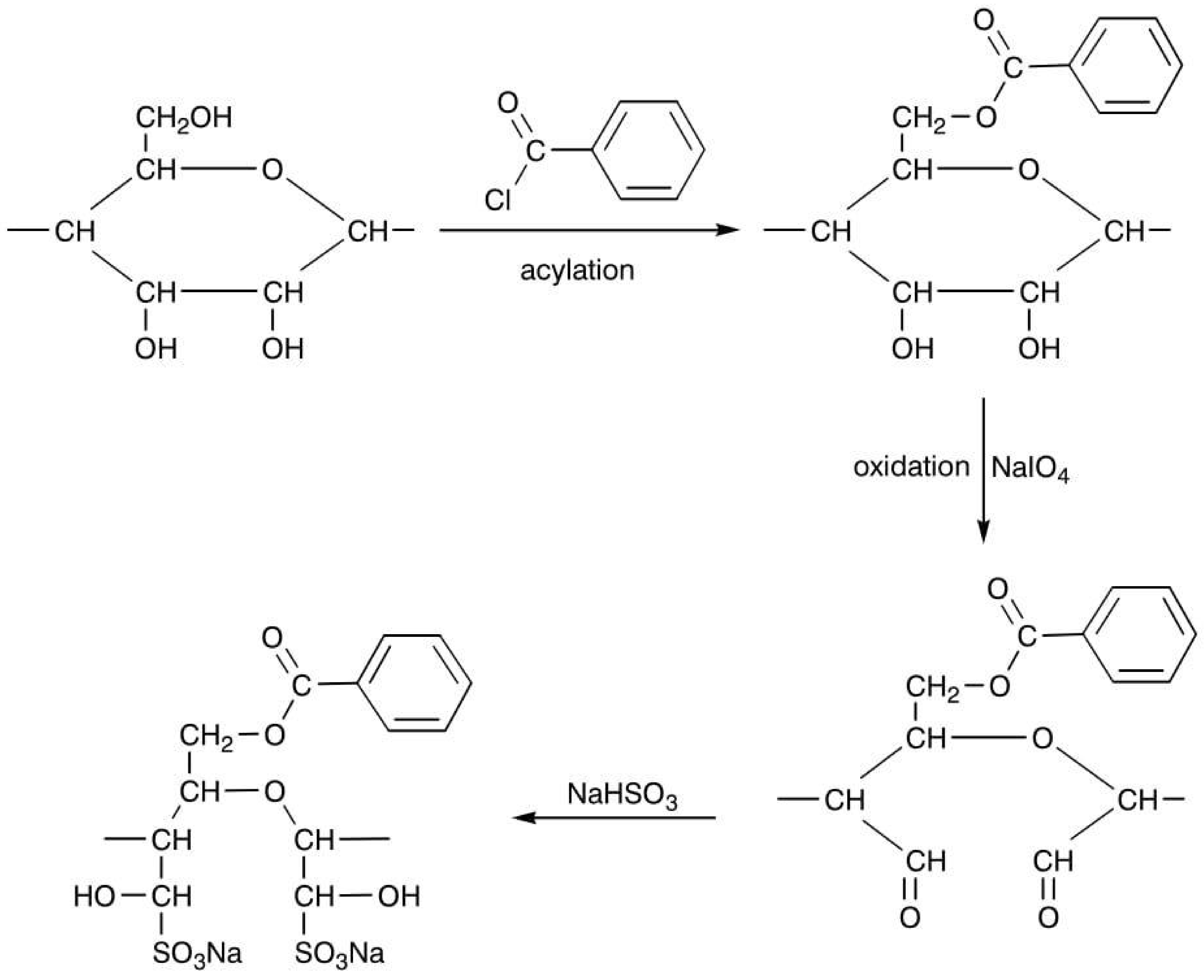
12.15

concluded that the following represented the optimal composition of a mixed auxiliary formulation:

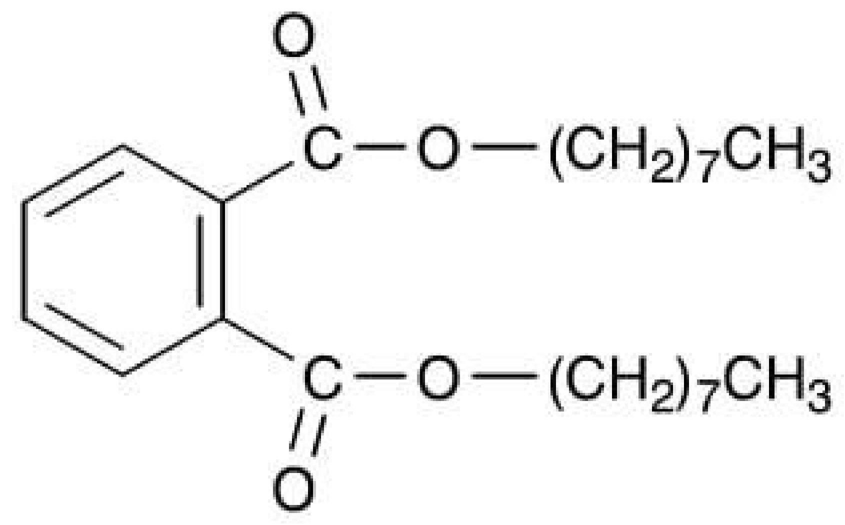
50% of a solubilising agent based on a branched-chain fatty alcohol with 8 units ethylene oxide per molecule
32% of a short-chain fatty alcohol with 2.5 units ethylene oxide per molecule
14% of a plasticising agent for acrylic fibres
12% of an ethoxylated long-chain alcohol (C_{10}–C_{18}) with 15 units ethylene oxide per molecule
12% of a short-chain fatty alcohol that increases the fixation of basic dyes.

In addition to the conventional dyeing of acrylic fibres, there is considerable interest in so-called gel dyeing of acrylic filaments during the manufacturing process after extrusion. From the viewpoint of auxiliary usage this is outside the scope of the present work, but a useful account of the factors involved is available [61].

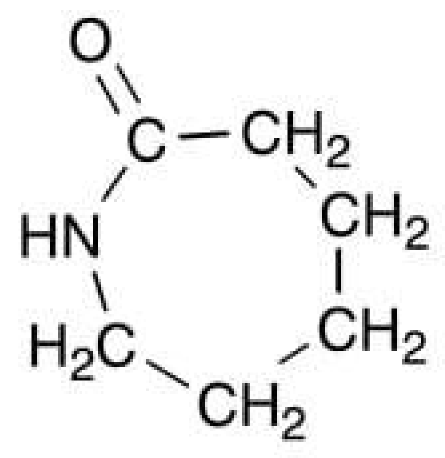
Basic dyes are used to dye acid-modified polyester fibres, in which case there is usually less need for a retarding agent. Glauber's salt is often added, however, to guard against hydrolytic degradation of these fibres [62]. Cotton modified according to Scheme 12.3 can then be dyed with basic dyes, although commercial exploitation of such a process is unlikely [63].



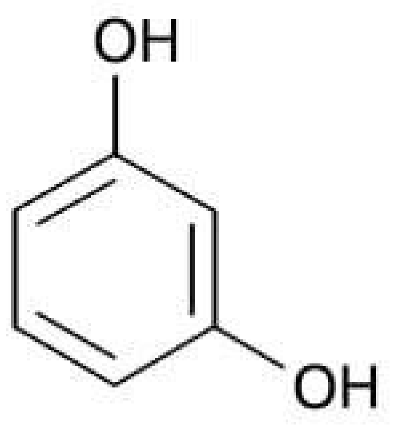
Scheme 12.3



12.16



12.17



12.18

In direct printing of acrylic fabrics a typical stock print paste [29] may contain the following components by mass:

0.5%	citric acid (12.7)
1–2%	dicyanoethylformamide (12.15)
3%	thiodiethylene glycol (12.5)
7%	acetic acid (30%)
50–60%	locust bean thickener

Dioctyl phthalate (12.16), caprolactam (12.17) and urea together with resorcinol (12.18) are also said to act as fixation assistants [64].A further addition of an anionic thickening agent such as carboxymethylcellulose [29] can act as a levelling agent when printing large blotches. A wash-off with anionic surfactant is usually given.

Discharge white styles are obtained using either formaldehyde-sulphoxylate or the weaker tin(II) chloride as reducing agent; crystal gum or British gum are recommended thickening agents, together with potassium thiocyanate as a fibre-swelling agent [29]. For coloured discharges tin(II) chloride is the recommended reducing agent, since formaldehyde-sulphoxylate would reduce the illuminant basic dyes; other additions are generally as for direct printing. Discharge styles, after steaming and rinsing, are given a clearing treatment at 40 °C in 1 ml/l ammonia (25%) and 1 g/l sodium dithionite [29], followed by rinsing and soaping with anionic detergent at 60–70 °C.

Non-destructive partial stripping techniques for basic dyes on acrylic fibres are carried out at 100 °C (or higher if possible) using, for example, 1–10% o.w.f. anionic retarder and 1 g/l acetic acid (60%), or 1–5 g/l Marseilles (olive oil) soap. Destructive stripping requires acidified (pH 5.5–6.0) sodium hypochlorite, followed by an antichlor treatment in sodium dithionite or sodium bisulphite. In some cases a preliminary boiling treatment in 5 g/l monoethanolamine and 5 g/l sodium chloride is said to improve the effect of the stripping treatment.

12.5 DIRECT DYES

Direct dyes represent one of the simplest dyeing systems, usually requiring only an electrolyte as an essential auxiliary for their application. Nevertheless a surfactant may sometimes be added to assist wetting and levelling, as well as a sequestering agent, since many direct dyes are sensitive to hard water. Control of pH may also be desirable. Certain traditional dyes require aftercoppering as part of their application procedure, whilst it is usual to aftertreat direct dyeings to improve their wet fastness properties. The dyeing of polyester/cellulosic blends with direct and disperse dyes requires application at temperatures higher than 100 °C.

An up-to-date account of the application of direct dyes is available [30]. The main area to be considered in the batchwise application of these dyes is the use of either sodium chloride or sodium sulphate to promote exhaustion, although the sulphate can give rise to calcium sulphate deposits in hard water. Direct dyes vary enormously in their response to electrolyte; in general the more highly sulphonated dyes require greater amounts of salt. This is in line with the behaviour of dyes according to the universally used SDC classification [30,65,66], whereby dyes are allocated to three application classes. Class A dyes are generally the most soluble and least sensitive to salt, hence necessitating substantial additions of electrolyte to boost their low exhaustion values. It is advisable with class A dyes to add electrolyte to the rinsing water to inhibit the otherwise copious bleed-off of dye into the water. For this purpose magnesium sulphate may be more efficient than sodium salts since it can form the less soluble magnesium salt of the dye, but the acceptability of this will depend on whether magnesium can be tolerated in subsequent processing. Dyes in classes B and C are generally less soluble and are so responsive to electrolyte that salt must be added gradually over the dyeing cycle as otherwise the rate of strike will be so rapid as to give unlevel, poorly penetrated dyeings and there may even be salting out of the dye in the dyebath. More salt is needed in longer liquors, and for heavier depths.

Dyes having the same CI generic name but made by different manufacturers may also require different amounts of electrolyte to be added to the dyebath, according to the amount of electrolyte present in the commercial formulation. A typical instruction is to use from 0 to

20 g/l salt depending on the factors described above. Electrolyte may influence migration as well as exhaustion [67], an optimal concentration of electrolyte being found for maximal migration of class A and B dyes, whilst the migration of class C dyes decreases with increasing amounts of salt. As mentioned above, sodium chloride and sodium sulphate are the electrolytes most commonly used in practice and it is generally accepted that they exert their effect by means of the common ion effect. There is another aspect, however; electrolytes also modify the structure of water around the hydrophobic groups in dye molecules and around the surface of the fibre, creating a new order in solution as a result of solvation. This enables dye molecules to approach more closely to the fibre surface within the influence of short-range interactive forces [68].

Numerous electrolytes have been investigated in fact, although some of the research work is seriously limited by having been carried out with only a few dyes, sometimes just one. In an investigation of the relative effects of Zn, Mn, Cd, Sr, Al and Ce nitrates [68], it was found that the size of the cation, as well as its charge, played a part in the sorption process: saturation values and sorption rates increased with increasing size of the cation. A similar effect has been observed for the series: LiCl < NaCl < KCl [69], whilst in binary mixtures of these electrolytes [70] the larger cation has a strongly promotional effect on the activity of the smaller cation (Figure 12.4). It has to be admitted, however, that these experiments were carried out at temperatures lower than is typical in commercial dyeing with direct dyes.

Mention has been made above of the use of magnesium sulphate to prevent bleeding of class A dyes during rinsing. With carefully selected dyes [71], magnesium salts can effectively replace the conventional sodium salts during dyeing. An optional mixture of

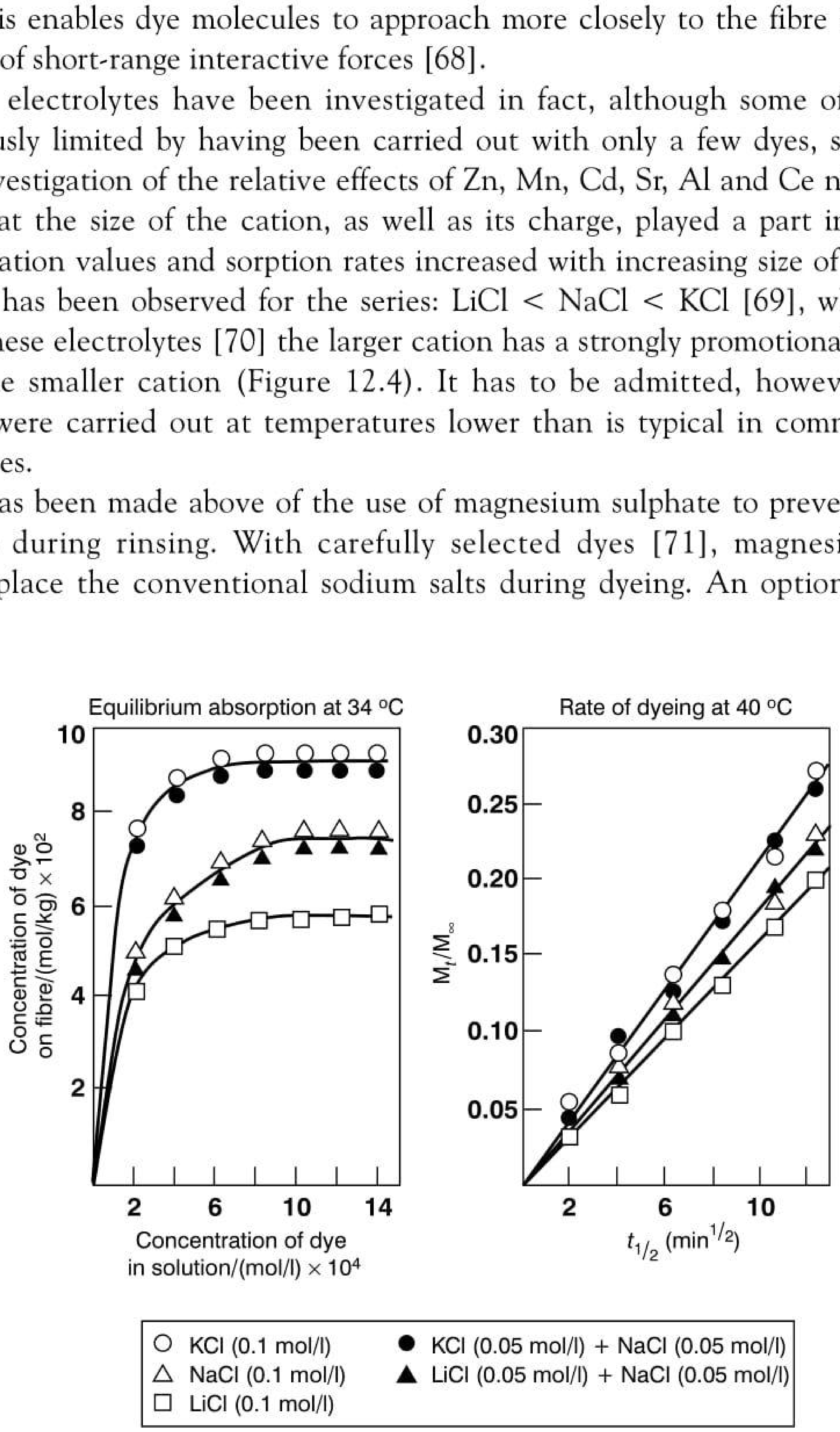


Figure 12.4 Equilibrium absorption isotherms at 34 °C and rate of dyeing curves at 40 °C for CI Direct Blue 1 on viscose in the presence of electrolytes singly and in binary mixtures [70]

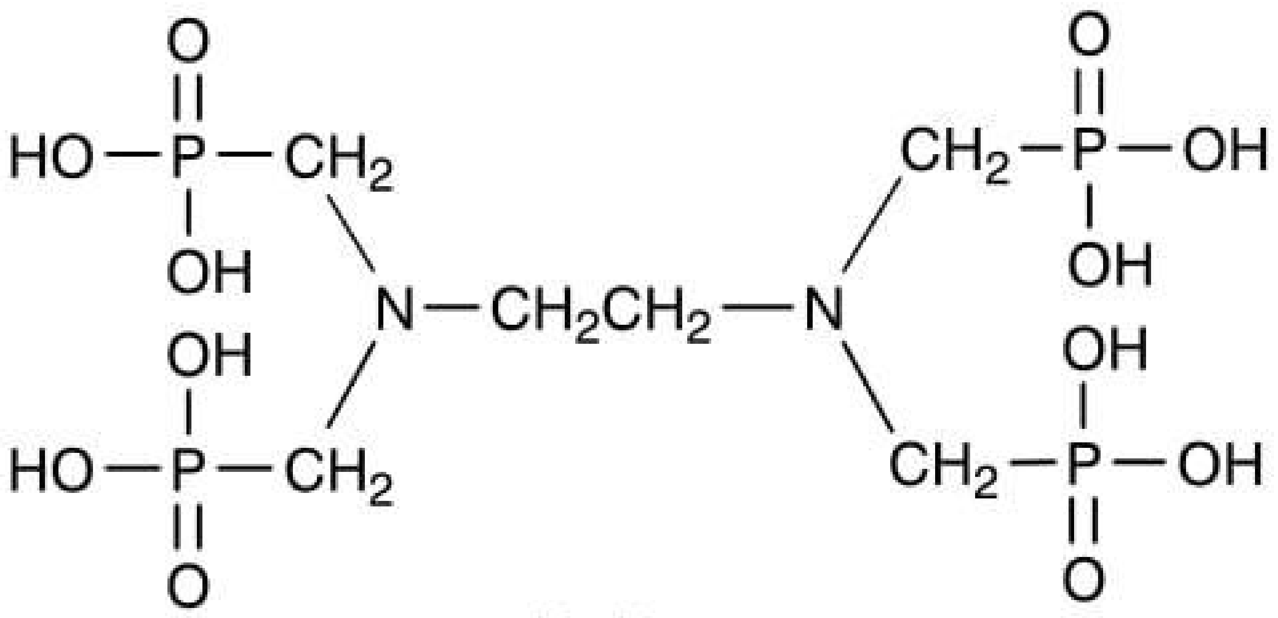
organic magnesium salts has been formulated. Since precipitation could be a problem, this proprietary mixture also contains a polymeric sequestrant. The rationale behind this process was to eliminate the conventional inorganic electrolytes from the dyeing process, since these have chronic toxic effects on freshwater organisms above certain concentrations. In addition, the usual electrolytes are quite difficult to remove from effluent. It is claimed that magnesium salts are used at lower concentrations and are easily removed from the effluent by precipitation.

For environmental reasons, other attempts have been made to reduce the amount of conventional electrolyte added. Lowering the liquor ratio will in itself reduce the amount of electrolyte required. In one commercially feasible system [72], a range of direct dyes was successfully screened to select members that could be applied efficiently to give 95–100% exhaustion using significantly less electrolyte than usual. Thus at applied depths up to 2–3%, only 2–5 g/l salt is required; navy and black dyeings can be produced with only 7.5–10 g/l salt compared with the conventional 25 g/l addition.

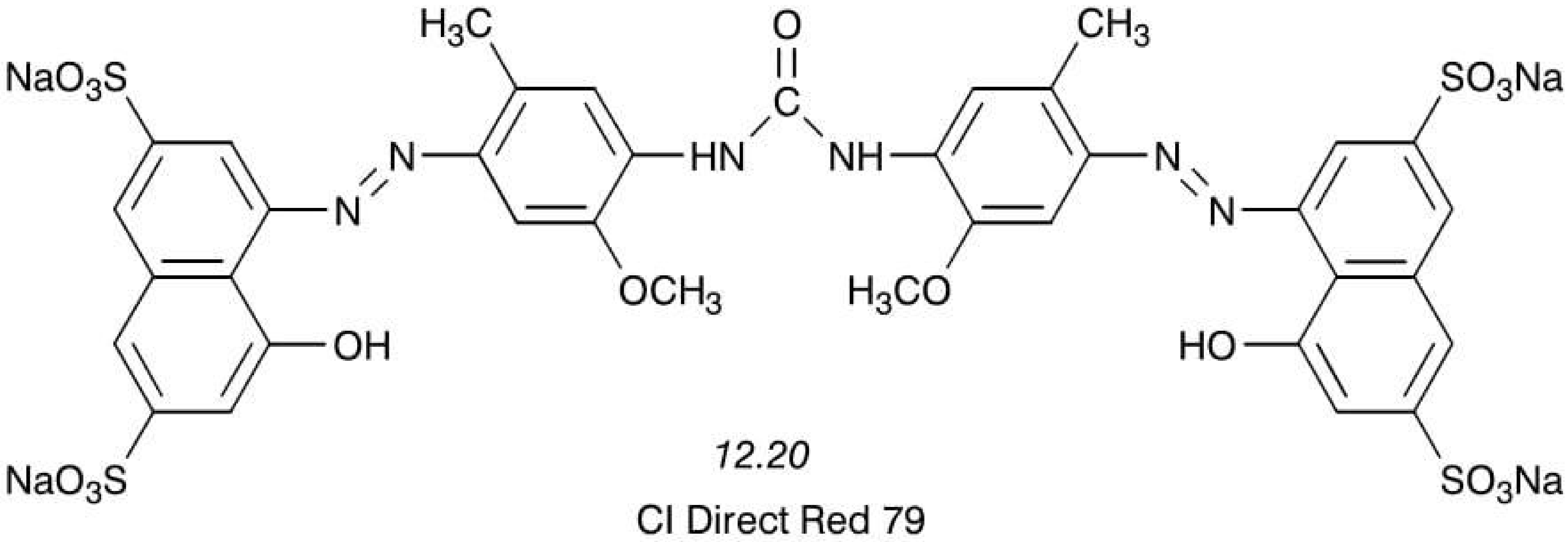
Ultrasonic irradiation has been shown in laboratory studies [73] to increase dye exhaustion, enabling salt levels to be reduced. However, it seems doubtful whether the higher effectiveness is sufficient to merit development to overcome the problems involved in scaling-up the ultrasonic equipment to bulk-scale processing. For example, in one experiment using 5% salt at 65 °C, ultrasound treatment increased the dye exhaustion from 77% to 82%.

A sequestering agent is usually necessary in hard water to prevent the formation of sparingly soluble calcium and/or magnesium salts. These can lead to uneven deposits of lower fastness on the surface of the fabric as well as reduced yields due to precipitation in the dyebath. Polyphosphates are particularly useful in this respect. Organic sequestering agents such as EDTA must be avoided with metal-complex direct dyes as they tend to extract the metal from the dye molecules, resulting in a change in hue and a significant lowering of fastness, although they can be used safely with unmetallised dyes. In a rather unorthodox approach to the use of sequestering agents, ethylenediaminetetramethylphosphonic acid (EDTMP; 12.19) applied as a pretreatment for cotton at ambient temperature was shown to increase the exhaustion of CI Direct Red 79 (12.20) applied at 100 °C in the presence of salt [74]. The maximum effect was achieved with 3 mg of sequestering agent per g of cotton. On dyeings carried out for 30 minutes, this gave surprising improvements in exhaustion from 35% to 45% (for 10 mg dye per g cotton) and from 17% to 29% (for 40 mg dye per g cotton). Rate of dyeing was apparently increased, too. Only this one dye and one sequestering agent were examined, however. It was found that about 35% of the tetraphosphonate was absorbed by the cotton. It was postulated that the phosphonate groups are only partially ionised in the neutral dyebath and that the presence of the nitrogen atoms favours hydrogen bonding between nonionised phosphonate groups and anionic sulpho groups in the dye molecule (12.21). Increased fastness to washing was also claimed [74].

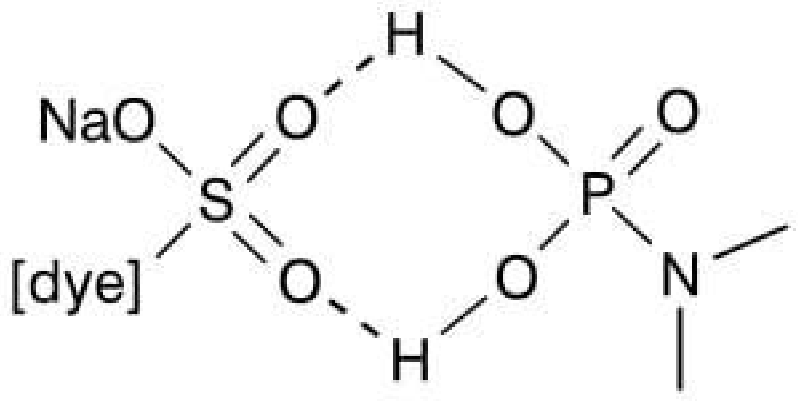
Some direct dyes are sensitive to reduction or hydrolysis under alkaline conditions, particularly if temperatures above 100 °C are used (section 3.1.3); pH 6 is frequently favoured for stability and this can usually be achieved using ammonium sulphate. A few dyes give optimal results under alkaline conditions, using sodium carbonate or soap; the tetraamino dye CI Direct Black 22 (12.22) is an example. Whether or not an addition is needed will depend on whether alkali is already present in the commercial brand.



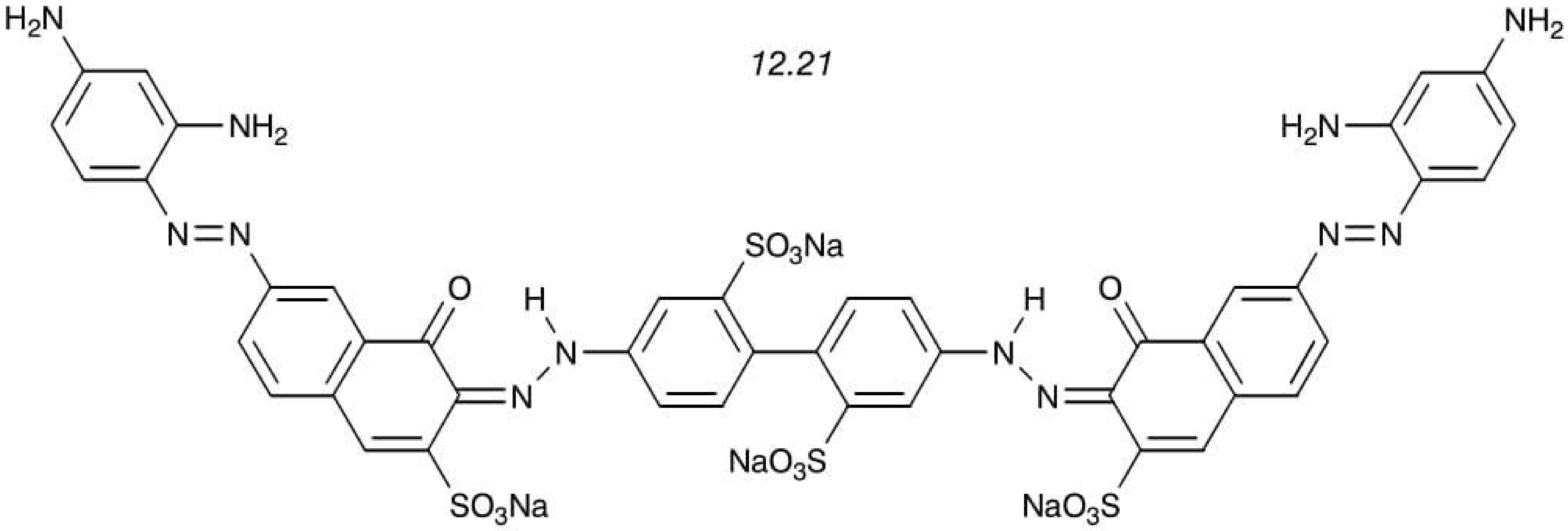
12.19
EDTMP



12.20
CI Direct Red 79



12.21



12.22
CI Direct Black 22

Levelling and wetting agents for direct dyeing are mostly ethoxylated adducts, such as alkylaryl ethoxylates, although anionic types such as alkylarylsulphonates, phosphate esters and alkylbenzimidazoles are also marketed. Care should be exercised in the use of such agents; there is spectrophotometric evidence [75] that they interact with dyes, leading to lower exhaustion. Since this interaction is dye-specific, there may be problems with mixtures of dyes. Such auxiliaries also add quantitatively to the COD value of the effluent [76]. Various other auxiliaries have been investigated but their commercial use is either limited or non-existent: urea, pyridine, amyl acetate, gelatin, carboxymethylcellulose [77]. Cyclodextrins [75,78] may have some potential for the future (section 10.3.1), although their action with direct dyes is dye-specific [75].

There is research interest in the potential to pretreat cotton with reactive compounds (section 10.9.1) followed by application of direct dyes or nucleophilic amino-containing dyes to give increased fixation and/or fastness. Attempts have also been made to apply such reactive compounds simultaneously with direct dyes [79]. Despite the inroads made by reactive dyes, there still remains considerable interest in the application of direct dyes, as evidenced by the introduction of the Optisal system by Clariant [80–82]. This is a carefully designed package of selected metal-free direct dyes, that require little salt to give high exhaustion and are stable up to 130 °C, together with a cationic formaldehyde-free fixation agent applied as an aftertreatment. The dyes may also be applied isothermally [81]. Environmental advantages are claimed, including high exhaustion, less pollution of effluent and low salt usage.

Various techniques are available for the application of direct dyes by semi-continuous and continuous methods, such as pad–jig, pad–batch, pad–steam, pad–dry and pad–thermofix. The major problem arises from the high substantivity of direct dyes for cellulosic substrates, making it very difficult to avoid tailing problems. Hence concentrated brands of dyes having minimal electrolyte content are preferred; of these, the class B dyes offer better operating properties. The main methods of controlling uniform uptake remain careful selection of dyes for compatibility, speed of padding and the rate of supply of padding liquor. Low solubility of the dyes may also be a problem; use of a hydrotropic agent such as urea improves the solubility of certain dyes and may also improve fixation, particularly in dry fixation processes. The washing-off process after fixation may be combined with an aftertreatment to improve the wet fastness and avoid undesirable bleeding of dye. Treatment with durable-press resins and with cationic products, particularly of the multifunctional reactant type, is especially useful here. The aftertreatment of conventional direct dyeings to improve fastness to light and particularly to wet treatments, using copper(II) sulphate, formaldehyde, diazotisation and coupling techniques or cationic fixing agents, has been described in section 10.9.5 and will not be discussed further here.

An interesting, if little-used, method of overcoming dye substantivity problems at the padding stage involved the use of certain amines, particularly those containing carboxyl or hydroxy groups such as structure 12.23 [83], in combination with 1:1 copper-complex direct dyes. A low-stability amine–copper–dye complex was formed. The complex diffused readily into the fibre and reverted to dye and amine during steam fixation, the amine being subsequently removed during washing-off. Careful selection of the amine, or mixture of amines, was necessary to achieve the desirable balance of properties. It is interesting to compare this use of an amine and 1:1 metal-complex direct dyes with the similar requirement for such dyes in the much more recent Indosol (Clariant) process (section 10.9.5).

$$HOCH_2CH_2NHCH_2CH_2NHCH_2CH_2OH$$

12.23

Direct dyes are of limited interest for printing because of their restricted wet fastness, resulting in cross-staining of whites or pastel-dyed grounds when the prints are subsequently washed. Somewhat better results can be achieved by treating the prints after steam fixation with, for example, a cationic fixing agent, durable-press resin or, in the case of chelatable dyes, copper(II) sulphate as already described (section 10.9.5). Most azo direct dyes will discharge easily with reducing agents and can therefore be applied as dyed grounds for discharge print styles, although the limitations described above with regard to wet fastness are especially pertinent here.

Partial non-destructive stripping of untreated direct dyeings can be accomplished with an alkaline solution of soap or synthetic detergent. Destructive stripping using a reducing agent such as sodium dithionite is also effective except with stilbene-type dyes. Aftertreated dyeings may additionally require a treatment to counteract the aftertreatment; for example, coppered dyeings can be treated with a sequestering agent such as EDTA and dyeings treated with a simple, non-reactive cationic agent may respond to treatment with an anionic detergent.

12.6 DISPERSE DYES

Disperse dyes as a class are peculiarly sensitive to the influence of auxiliary agents, both as regards the quality and stability of the dispersion and the response of the dyes during the various coloration processes. Essential auxiliaries in batchwise dyeing include dispersing agents and chemicals to control the pH. Supplementary auxiliaries termed ‘carriers’ may be needed under certain circumstances to accelerate the otherwise inadequate rate of dyeing. Aftertreatment of the dyeings to remove surface dyes is important in many cases, as are the conditions of drying and finishing since these can influence fastness properties.

12.6.1 Dispersing agents

The essential chemistry of dispersing agents has been discussed in section 10.6.1, where it was noted that different considerations may apply at the comminution stage of dye formulation compared with maintaining the stability of the dispersion during subsequent coloration processes. The dyeing of polyester at a temperature in the region of 120–135 °C in beam and package dyeing machines places severe demands on initial dispersion quality and subsequent stability under adverse conditions. Jig dyeing with a high concentration of dye in a very short liquor (as for navy blues and blacks) can also be the source of dispersion stability problems.

The crux of the problem lies in the inherent thermodynamic instability of all dye dispersions, there being an overall tendency of fine particles to undergo Ostwald ripening with the consequent formation of larger particles. Although disperse dyes are generally considered to be virtually insoluble in water they are, in colloidal terms, sparingly soluble; indeed a low degree of solubility seems to be a necessary prerequisite for dyeing to take place from an aqueous medium. It is this limited solubility that favours Ostwald ripening. The detailed colloid chemistry of dispersions with particular reference to these phenomena has been thoroughly discussed [84]. The solubility of disperse dyes normally increases with temperature and dispersing agent concentration, although these effects vary enormously from agent to agent and from dye to dye.

Most dispersing agents are of the anionic polyelectrolyte type, comprising various sulphonated condensation products of aromatic compounds and lignosulphonates (section 10.6.1). Increasing understanding of lignin chemistry with consequent improvements in manufacture, enabling lignins to be more economically and reliably ‘tailored’ for specific end-uses, currently favours the use of these products, although by no means exclusively. Solid brands of disperse dyes contain a significant proportion of dispersing agent added during formulation; liquid brands contain rather less as they do not have to withstand the thermal and mechanical rigours of spray drying [85] and do not require redispersing at the dyebath preparation stage. Despite this, it is still advisable to add extra dispersing agent at the dyeing stage, more being required with liquid dyes to compensate for their lower intrinsic content. At the grinding stage of dye manufacture lignosulphonates with a high degree of sulphonation generally perform better. Less sulphonated types tend to give better stability at high dyeing temperatures [86], since they are more readily adsorbed onto and retained by the hydrophobic surfaces of the dye particles.

The complexity of the relationships within a disperse dye system is well illustrated in Figure 12.5. The particle size distribution in a disperse dyebath and any transformations taking place during dyeing, including the three successive phases of heating up, maintaining top temperature and subsequent cooling, can exert critical effects on rate of dyeing, final degree of sorption and levelness. Whilst microscopy techniques are undoubtedly useful in studying dispersions, much more detailed information is obtained from photon correlation spectroscopy using a Coulter counter [88]. Figure 12.6 shows an example of particle size

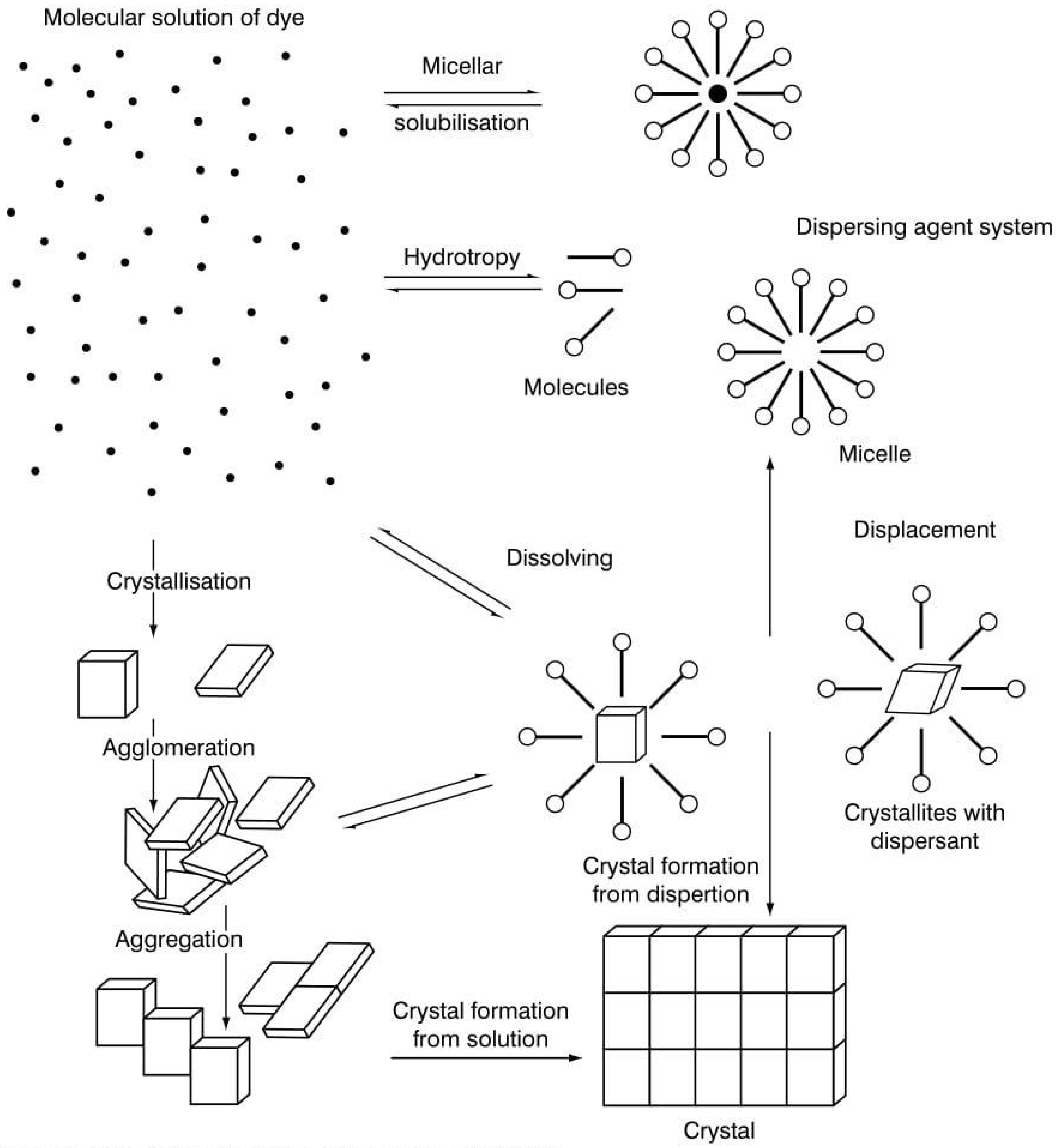


Figure 12.5 Model of the disperse dye system [87,88]

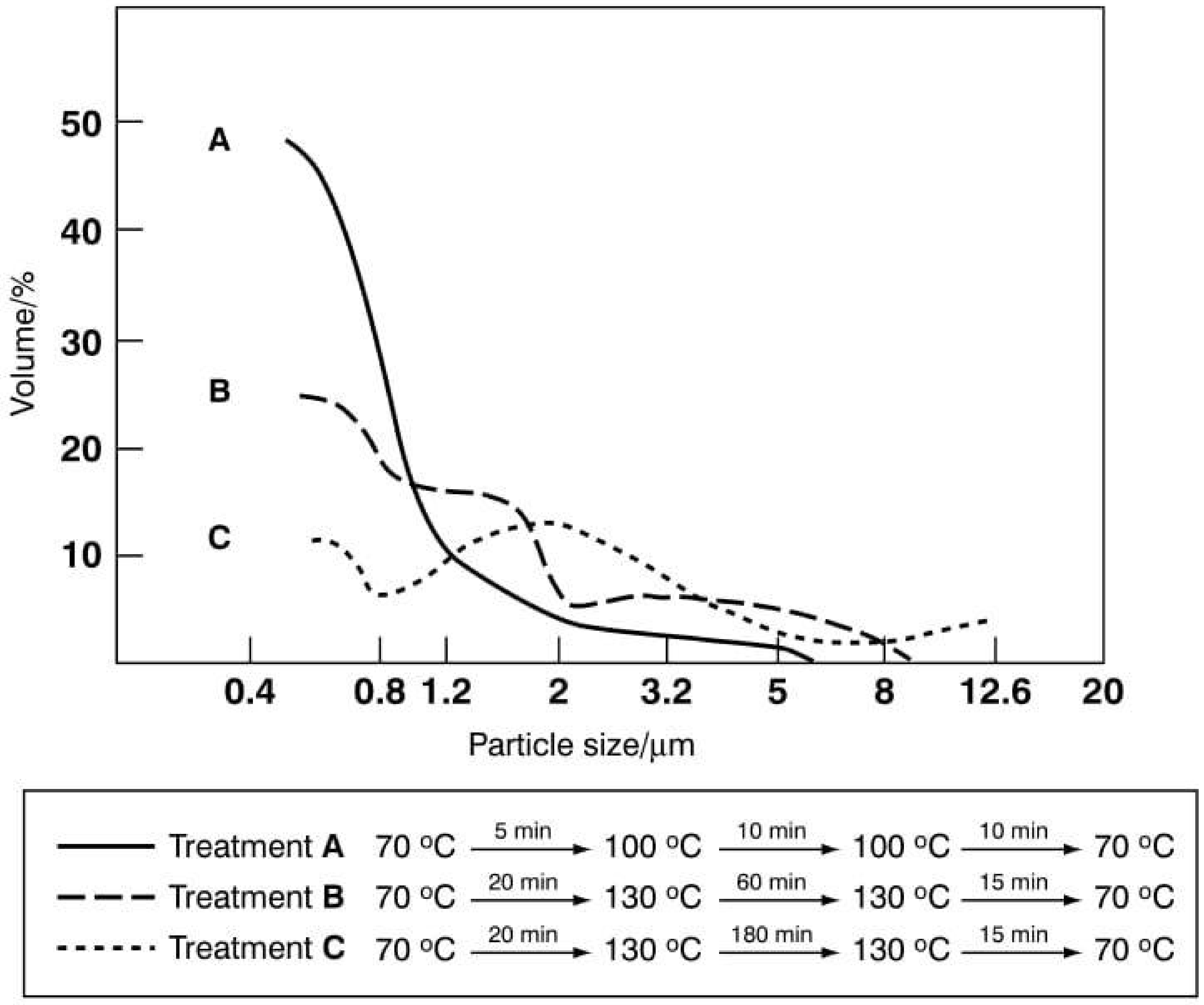


Figure 12.6 Effect of temperature changes on the particle size distribution in a dyebath containing 0.6% CI Disperse Orange 13 [88]

transformations taking place in a specific dispersion of CI Disperse Orange 13 on exposure to three different temperature profiles.

The addition of auxiliaries, such as additional dispersing agents, levelling agents, carriers and electrolytes, brings about further changes that may be beneficial or otherwise, depending on circumstances. A method based on a ternary diagram (Figure 12.7) representing the relationship between dyeing properties and the concentrations of three dispersing agents used simultaneously in the dyebath has been described [89]. Of course, any ranges of concentration can be chosen that are appropriate for the dispersing agents present. The scheme is suitable not only for studying particle size distribution using a laser particle sizer as in this instance, but also for examining effects such as solubilisation, rate of dissolution, diffusion coefficient, dyeing rate and colour difference. Figure 12.8 shows how these various factors can be compared in a single diagram [89].

An alternative approach to evaluating the efficiency of dispersing agents depends on the partition effect [90]. In this simple and practical method a sample of the aqueous dispersion is extracted with a water-immiscible solvent (e.g. chloroform, methylene dichloride, monochlorobenzene, dimethyl phthalate, tetrachloroethylene) in which the dye but not the dispersing agent is soluble. Unprotected disperse dye particles dissolve immediately in the solvent layer. Dye particles protected by a sheath of dispersing agent are more hydrophilic and therefore favour the aqueous layer. The rate of extraction of a disperse dye from the aqueous layer into the solvent depends on the stability of the dispersion and the extraction conditions. However, there must be limits to the applicability of this method to the study of phase transitions during the dyeing process.

The influence of dispersant structure on the thermal stability of dye dispersions has been illustrated as in Figure 12.9. Thermal stability appears to be related to the relative numbers and strengths of the adsorbing and stabilising groups in the dispersing agent. Partial blocking

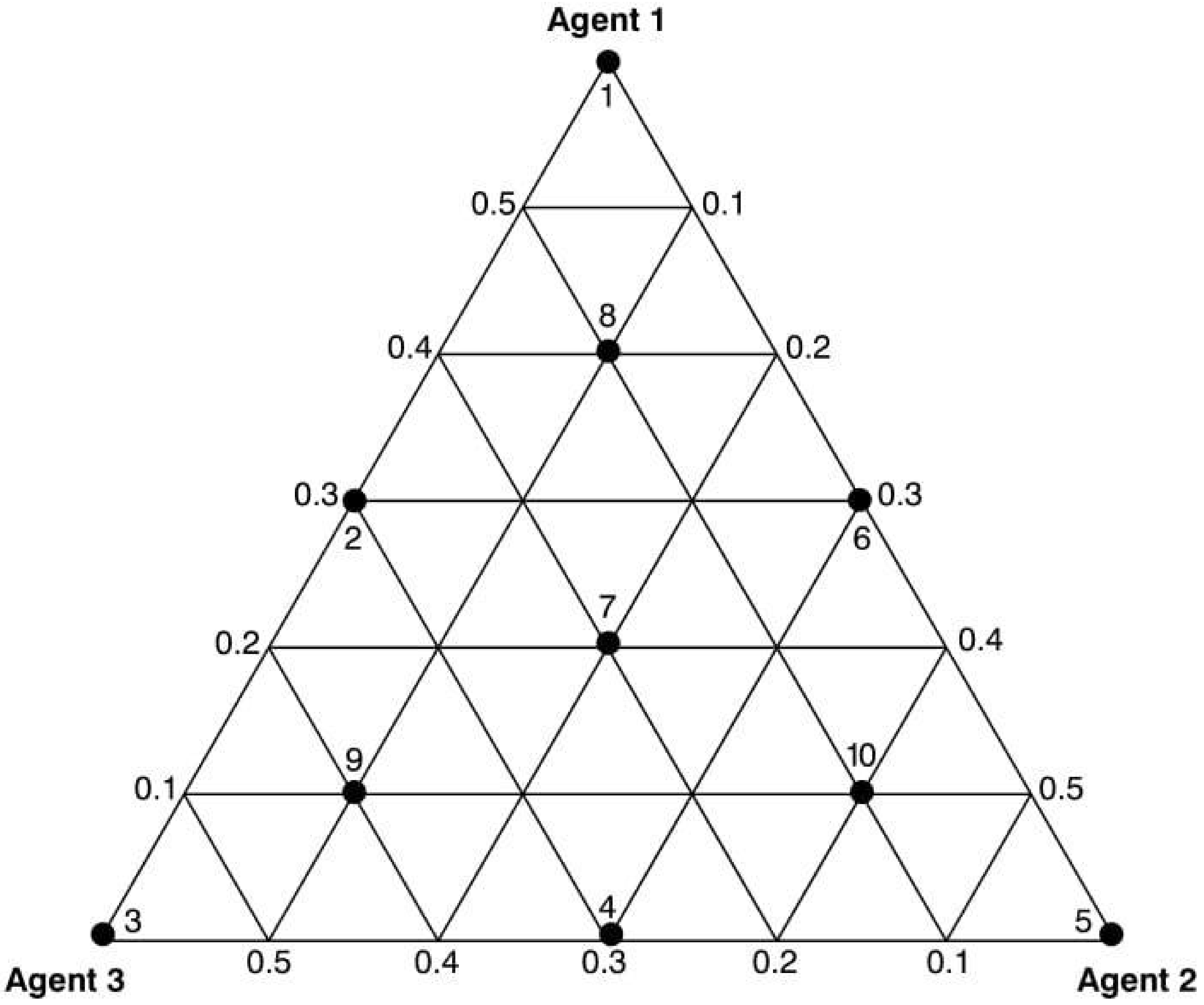


Figure 12.7 Basic points of the ternary diagram in which individual parameters were determined experimentally; agent concentrations are quoted in g/l [89]

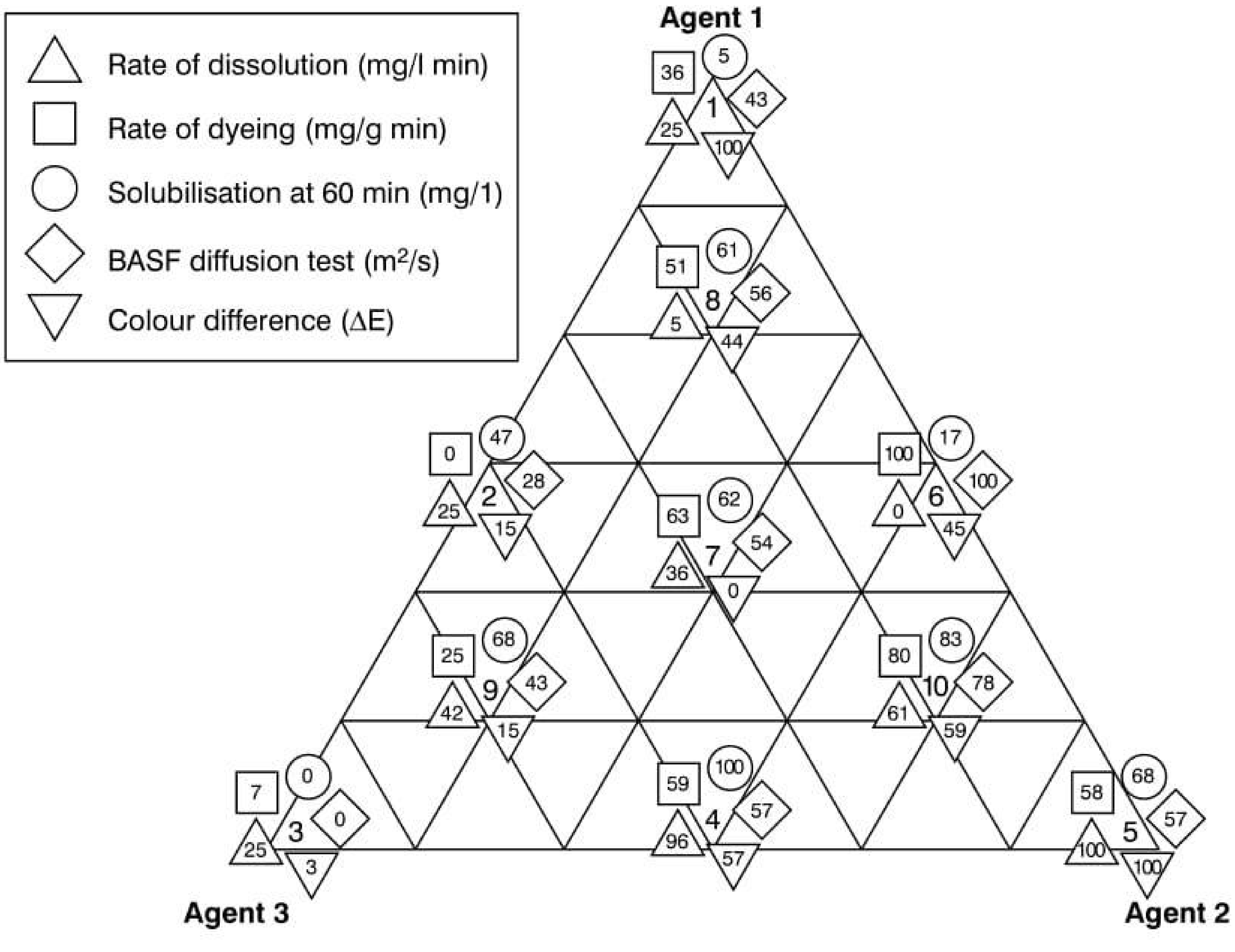


Figure 12.8 Overall dependence of observed parameters in dyeing with CI Disperse Orange 21 in the presence of a mixture of three agents [89]. The value within each symbol represents a percentage of the maximal effect (= 100%) for that factor

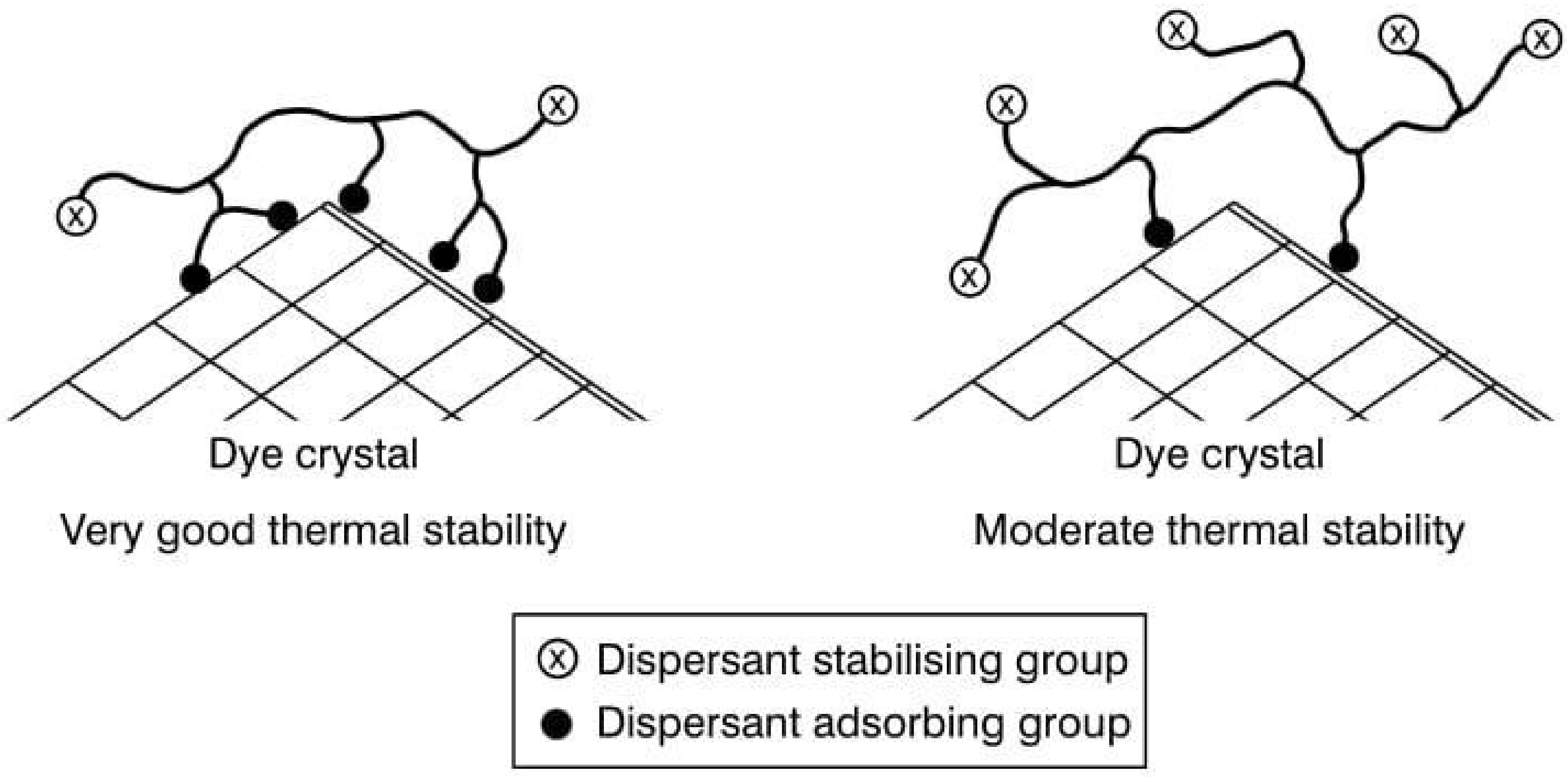


Figure 12.9 Dependence of dispersion thermal stability on dispersing agent structure [91]

of phenolic groups in a lignosulphonate, for example, reduces the thermal stability by an amount that corresponds quite well with the lower concentrations of residual phenolic and carboxyl groups. The degree of adsorption can be determined by equilibriating a known mass of dye with a surfactant solution of appropriate concentration at constant temperature. The dye particles are then separated by filtration or centrifugation, followed by UV analysis of the supernatant liquid to determine the concentration of dispersant remaining. The amount of surfactant adsorbed per gram or per unit area of the dye particles is then calculated from the difference between the initial and final concentrations of the surfactant [91].

From the environmental viewpoint there are two important problems associated with dispersing agents:

(1) dustiness of powder brands
(2) inadequate and slow biodegradability.

Since disperse dye powders supplied to the dyer have been treated already to render them essentially non-dusting, dustiness problems are mainly of concern during dye manufacture [92]. Nevertheless, some dyes remain inadequately treated, or after an initially adequate treatment they may deteriorate during storage, thus giving rise to hazards in handling associated with excessive dustiness. Methods of assessing dustiness have been reviewed [92].

Since dispersing agents are not significantly absorbed by the fibre, they remain in the exhaust dyebath and are discharged to effluent. As a result of their polymeric nature and the presence of stable benzenoid rings, most lignosulphonate and formaldehyde-naphthalenesulphonate dispersing agents are only bioeliminated to about 30% [92–94]. They may also contain small amounts of residual starting materials that are toxic to fish [92]. More complete elimination can be achieved by precipitation with heavy metal salts or cationic surfactants, but this leads to problems of disposal of solid wastes. Dispersing agents based on mixtures of sodium salts of arylcarboxylates are claimed to offer superior bioeliminability (70%) and to show markedly improved application properties compared with traditional dispersing agents [93,94].

Dyebath pH exerts a marked influence on the efficacy of lignosulphonate dispersing agents, since this factor determines the degree of dissociation of phenolic and carboxylic acid groups, influencing the extent to which they are able to interact with the dye molecule. In general, the lowest pH that can be tolerated by the system (dye, fibre and auxiliaries) tends to give the greatest dispersion stability during heating of sodium lignosulphonates [91]. The situation is somewhat different with amine salts of lignosulphonates, since these differ from the sodium salts in their degree of ionisation. For example, when the pH is lowered from pH 7 to 4, more amino groups are protonated, thus increasing the proportion of ionised sulphonate groups present. The solubility of the dispersant is increased and so the adsorption of agent by the disperse dye particles becomes more difficult. However, the overall situation is complex because lignin derivatives vary in their content of phenolic and carboxylic acid groups and these exhibit a range of pK_a values according to their location within the macromolecule.

Some azo dyes are susceptible to reduction under unfavourable conditions [95]. The least stable dyes tend to be those containing electron-withdrawing groups, such as nitro, chloro or cyano, *ortho* to the azo linkage. This instability to reduction is minimised by dyeing at the optimal pH, usually pH 4–5, in the presence of air, and by minimising the dyeing time at high temperature. Hence, under appropriate conditions, instability is not a serious problem. Decomposition is favoured, however, by various factors:

(1) pH values greater than 6
(2) the absence of air (anaerobic dyeing conditions)
(3) the presence of fibres containing reducing groups, such as wool or cellulose
(4) the presence of reducing metal ions, such as copper(I) or iron(II), in the water supply
(5) dispersing agents containing phenolic groups
(6) conditions that tend to maintain the dye for longer periods in the liquor, such as slower-dyeing substrates (low-porosity sewing threads, for example) and auxiliaries that tend to solubilise the dye too much.

Lignosulphonate dispersing agents tend to promote this reduction of sensitive dyes, much more so than the naphthalenesulphonic acid condensation types, probably owing to the presence in lignin of catechol residues and other easily oxidised functional groups [95] (structures 10.104 and 10.105). Commercial lignins vary considerably in their detailed constitution, however, and consequently in their reducing power. In certain cases the problem can be ameliorated by adding an oxidising agent (such as sodium dichromate) to the dyebath, but the effects can be variable and difficult to control. In printing applications, where steam fixation can have a pronounced reductive effect, stronger oxidising agents such as sodium chlorate are often added to the print paste. In theory the reductive tendency of lignosulphonates can be counteracted by chemical blocking of the active phenolic groups but this impairs the dispersing properties of the product [91,95]. Significant improvements can be achieved by replacing the conventional sodium ion in the lignosulphonate salts by other cations [91]; lithium is effective in this respect, but the most promising salt appears to be that of triethanolamine. This compound additionally acts as a chelating agent and so protects against the catalytic influence of iron(II) and copper(I) ions.

Since high concentrations of electrolyte can adversely affect dispersion stability, low-salt formulations of dispersing agents have been developed [95]. These also help to minimise the lowering of viscosity by electrolytes with certain synthetic thickening agents in printing applications.

In some cases it is necessary to choose dispersing agents that give minimal staining of the substrate. This applies particularly when dyeing nylon since anionic dispersing agents have significant substantivity for this fibre under acidic conditions. In general, lignosulphonates have a greater propensity to stain than have the naphthalenesulphonic acid condensation products.

12.6.2 pH control and sequestering agents

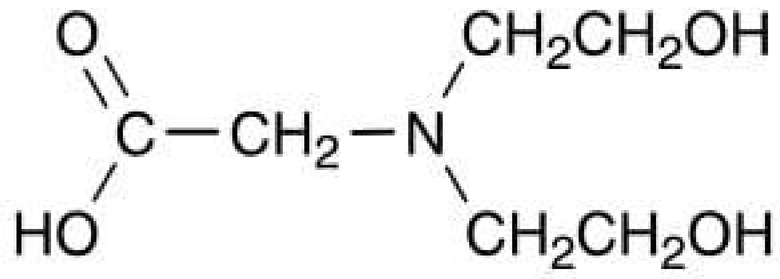
Although many disperse dyes give good results over an extensive pH range (pH 2–9 for example), some will only give satisfactory results over a narrower acidic range (pH 2–6) and a few require careful control to within pH 4 to 5.5. Since practically all dyes give good results at pH 5, this region tends to be regarded as the standard for exhaust dyeing conditions. A simple addition of acetic acid will be satisfactory where water quality permits; otherwise a buffered system is preferred. EDTA (section 10.2.1) is widely used to counteract the effects of metallic impurities, which not only affect the hue and fastness of a few susceptible dyes but may also catalyse dye reduction and promote deterioration of dispersion properties, as described above.

In spite of the traditional preference for dyeing at about pH 5, the past decade has seen the promotion of polyester dyeing methods under alkaline conditions at pH 9.0–9.5 [96–98]. Various advantages are claimed for alkaline dyeing conditions. These include the benefits of economy and convenience that arise from dyeing at a pH closer to those used in preparation, including bleaching, mercerising of polyester/cotton and caustic weight reduction of polyester, as well as the clearing of surface dye after dyeing. This approach may eliminate the need for neutralisation or slight acidification after alkaline treatments. Further advantages claimed include improved handle of the substrate, more effective solubilisation and removal of oligomer, less frequent and easier cleaning of machinery and possible avoidance of reduction clearing. Alkaline conditions facilitate the simultaneous application of disperse and reactive dyes to polyester/cellulosic blends.

Apart from the essential primary requirement of selecting disperse dyes that are stable to pH 9.5 at least, or preferably higher to ensure a safety margin, the choice of auxiliaries for this process is critical. The main requirement is a buffer system having sufficient reserve capacity to maintain pH 9 throughout most of the dyeing process. This is more difficult than might be assumed, since the polyester fibre and the oligomers present are partially hydrolysed by alkali at a high dyeing temperature to form carboxyl and other groups that cause a gradual lowering of the pH. Consequently, dye manufacturers have introduced alkaline dyeing ‘packages’ comprising a selected range of stable disperse dyes together with a purpose-designed auxiliary system to maintain the required pH. Little has been published about the detailed composition of such systems. However, they are claimed to contain more than just a suitable buffering system. For example, one such auxiliary is claimed [96] to be designed to (a) stabilise the dyes, (b) provide adequate buffering, (c) chelate metal ions and (d) assist dissolution of oligomers, whilst a second auxiliary is offered for use where there is an unusually high content of oligomer.

Attention must be given to dispersion stability and to oligomer control. This is because certain types of dispersing agent have inferior efficiency under alkaline conditions and more oligomer is released into alkaline liquors. Unless the oligomers are adequately dispersed or solubilised they may contribute to dye dispersion problems and may be deposited onto the fibre or machinery. Hence, careful thought must be given to the selection of dispersing or solubilising agents.

With regard to the buffer system, an extensive range of amino acid derivatives applied in combination with an alkali have been claimed [99]. From this extensive list, primary preference is given to *N*,*N*-bis(hydroxyethyl)glycine (12.24) in combination with sodium hydroxide. However, *N*,*N*-dimethylglycine, *N*-methylglycine and *N*-methylalanine are also listed as preferred compounds, whilst other possible alkalis include sodium carbonate, sodium bicarbonate or borax. Another system depends on the formulation of a mixture of a phosphonate and a polycarbonic acid in combination with sodium hydroxide, borax, sodium carbonate or bicarbonate [100]. Whichever buffer system is used, extensive empirical trials are required to determine the balance and concentration level needed to ensure stability of pH during the specific conditions of use.



12.24

12.6.3 Electrolytes

Electrolytes are unnecessary for the application of disperse dyes alone. Nevertheless, electrolytes will be present when applying disperse dyes together with direct or reactive dyes in the dyeing of fibre blends. In particular, the high concentration of salt often used with reactive dyes can have an adverse effect on dispersion stability and may also interfere with the stability and/or efficacy of other auxiliaries, particularly those based on emulsion systems. These effects are often attributed to the destabilising influence of inorganic ions on the forces of attraction between disperse dye particles and dispersing agents. Manufacturers take these effects into consideration in marketing 'electrolyte-stable' formulations of disperse dyes or auxiliaries.

12.6.4 Levelling agents

It is necessary to distinguish clearly between levelling agents and dispersing agents. The primary function of a dispersing agent is to maintain a stable dispersion. Since most of these agents enhance the low water solubility of disperse dyes they may improve level dyeing, although they vary significantly in this effect. Maximal dispersion stability is usually attained with agents that maintain dye particles at constant size and minimal solubility. Hence primary dispersing agents seldom enhance levelling; different auxiliaries are added where levelling action is needed. These are invariably anionic or nonionic surfactants and they tend to solubilise the dye much more effectively. Some anionic levelling agents are able to promote dispersion stability but nonionic types have a destabilising effect and great care is therefore required in selection.

It is useful to consider how levelling agents can adversely affect dispersion stability. As dyebath temperature increases, thermal effects tend to cleave the film of dispersing agent protecting the dye particles. High shear rates in jet dyeing machines and additives such as electrolytes, fibre lubricants or sizes, as well as oligomers from the fibre, can contribute to this effect. Commercial batches of the same dye brand may behave differently according to the initial dispersion quality of the dye. A dispersion of a vulnerable dye then tends to deteriorate, resulting in crystallisation and agglomeration. The types of precipitation that can occur have been described [87,88,101] and are illustrated diagrammatically in Figure 12.5 (section 12.6.1).

Suspended dye crystallites tend to agglomerate, eventually forming larger crystals. The dissolved dye molecules are able to diffuse into the fibre, but under adverse conditions crystallisation is favoured. Once seeded, the crystals may grow in size whilst retaining their original form, or they may undergo a transformation from the original thermodynamically metastable form to a more stable but less soluble form. On the other hand, such crystals may not form until the incompletely exhausted dyebath is cooled after the dyeing process; this problem may be avoided by blowing off the dye liquor at 125–130 °C. Precipitation by agglomeration tends to predominate with those dispersing agents that do not enhance dye solubility significantly, whereas crystallisation is more prevalent with levelling agents or dispersing agents having greater solubilising power. It is interesting that surfactant additions may be used during dye synthesis in order to obtain the dye in the optimal form for isolation and subsequent milling; for example, very fine crystals may clog filters, whilst thin needle-like crystals tend to mill more easily than platelets.

Anionic levelling agents, especially the polyelectrolyte dispersing agents described previously, are generally preferred as the primary addition [102], particularly where it is desired to promote level dyeing by control of exhaustion during the heating phase of dyeing; higher concentrations have a greater retarding effect. Few of these anionic products promote dye migration, a characteristic that is useful if a more powerful levelling action is required.

Nonionic surfactants, on the other hand, tend to solubilise the dye much more effectively and thus contribute to level dyeing both by a retarding effect and through the promotion of migration. Consequently they are generally more powerful levelling agents than anionic products although their effects are much more dye-specific. The dye-specific effects on retarding and restraining have been well-publicised [103–107], although the full extent of the variations is often overlooked in the industry. The restraining effects of a typical nonionic agent, a nonylphenol with an average of 20 ethylene oxide units per molecule, on five commercially important disperse dyes are illustrated in Figure 12.10. The spread of results between CI Disperse Blue 56 (only slightly affected) and CI Disperse Yellow 42 (much more affected) should be noted. Other nonionic auxiliaries would yield different effects and dyes may behave differently in mixtures compared with their response when tested in isolation. The retarding effects of the same agent on CI Disperse Blue 56 and Yellow 42 applied as a green 1:1 mixture are shown in Figure 12.11.

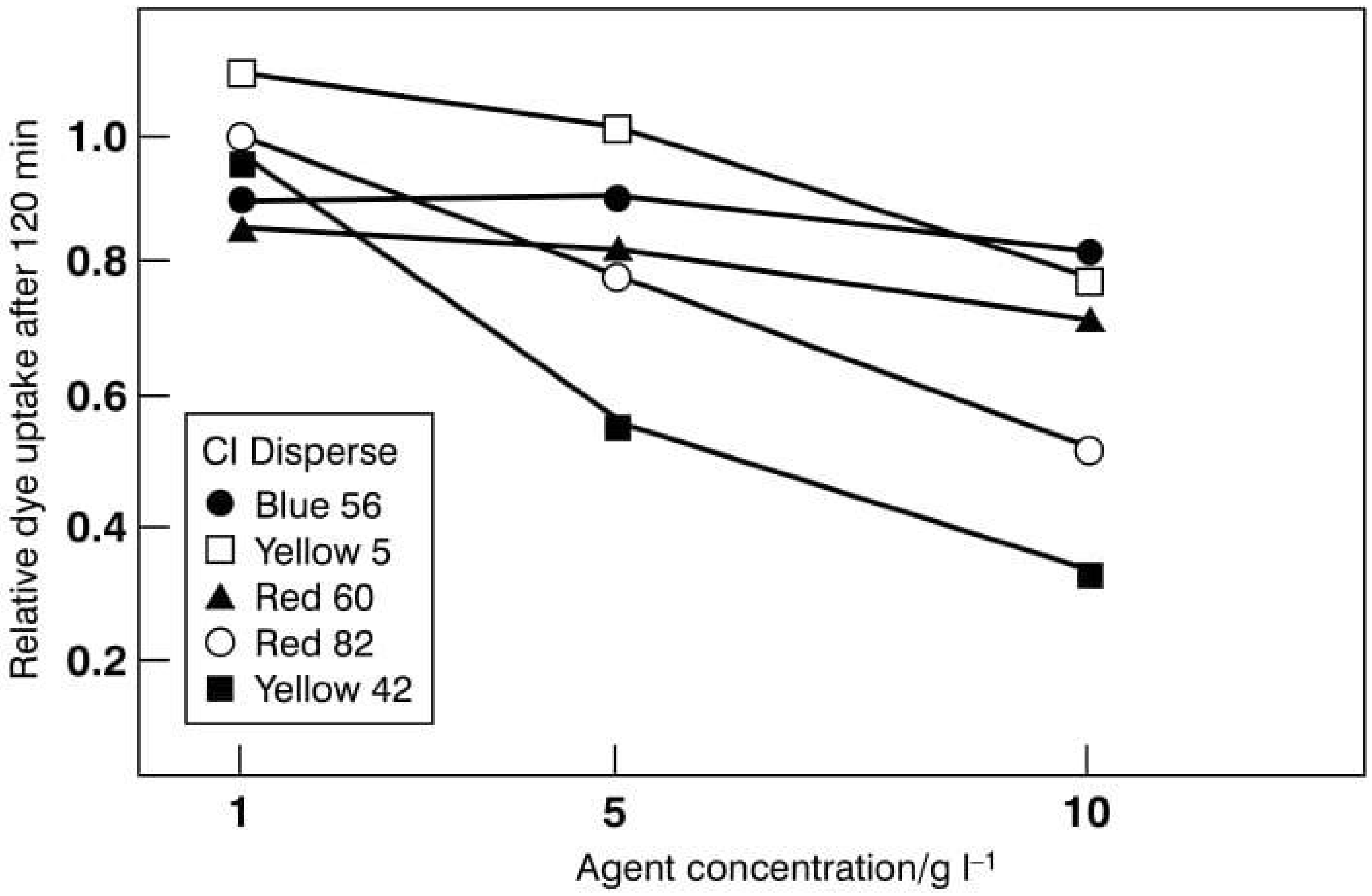


Figure 12.10 Relative dye uptake values for five disperse dyes on polyester at various concentrations of a nonylphenol 20 EO levelling agent [107]

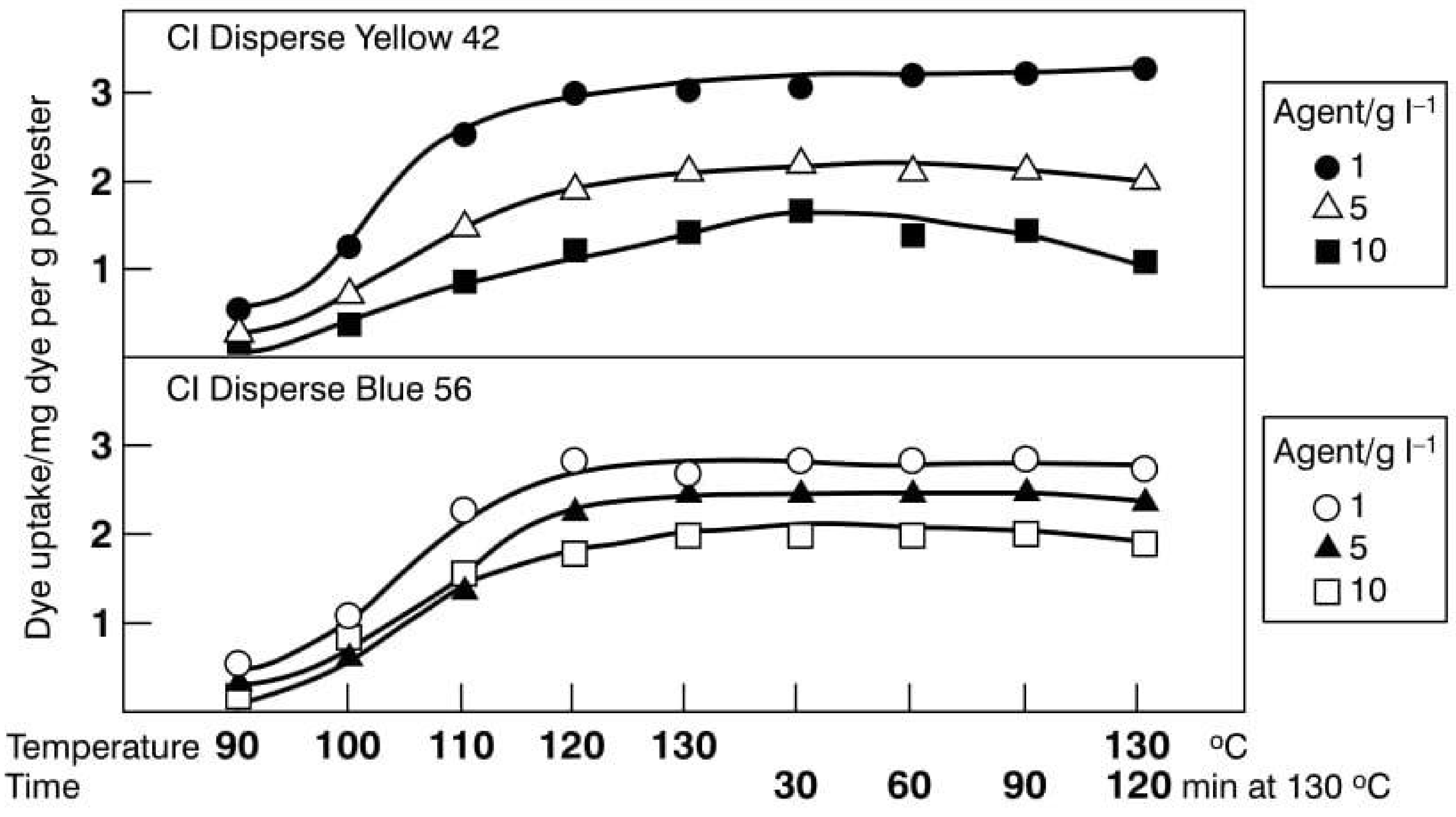


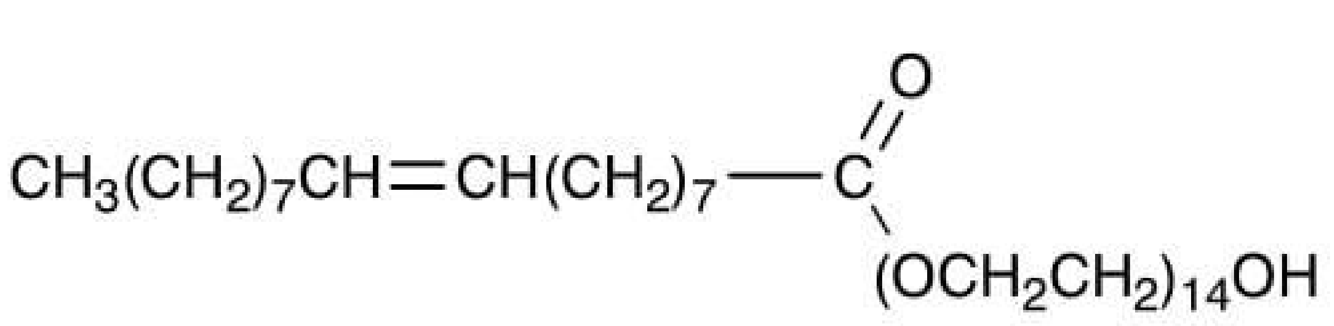
Figure 12.11 Rate of dyeing curves for CI Disperse Blue 56 and Yellow 42 in admixture on polyester at various concentrations of a nonylphenol 20 EO levelling agent [107]

This complexity of response has critical implications for reproducibility of dyeing, particularly within the context of right-first-time dyeing. Careful prior evaluation and optimisation of each recipe, followed by consistent bulk use and monitoring, are essential for good reproducibility. Instrumental colour difference measurements are particularly useful for evaluating and monitoring responses [107,108]. On the other hand, a study of four different polyethoxylated sorbitan esters indicated that there were no significant differences between them in terms of desorption of disperse dyes from polyester [109]. Desorption, however, is only one aspect of level dyeing and migration.

A major problem with nonionic agents arises from their inverse solubility. Thus an agent with a low cloud point may increase dye precipitation, although once again the effect is dye-specific. Published data suggest that a nonylphenol with a low degree of ethoxylation, having a cloud point of about 40 °C, should not be used as a disperse dye levelling agent [110]. A product of type 12.25, having a cloud point of about 105 °C, should be satisfactory for dyeing at any temperature up to 100 °C but should be avoided at higher temperatures. On the other hand, a carefully selected nonionic agent may be mixed with an anionic agent to raise its cloud point. For example, a mixture of the fatty acid ethoxylate 12.26 with 7–10% sodium dodecylbenzenesulphonate [110] has a cloud point of about 150 °C and is suitable for use in high-temperature dyeing.

$CH_3(CH_2)_{15}(OCH_2CH_2)_{17}OH$

12.25



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7{-}C({=}O)(OCH_2CH_2)_{14}OH$$

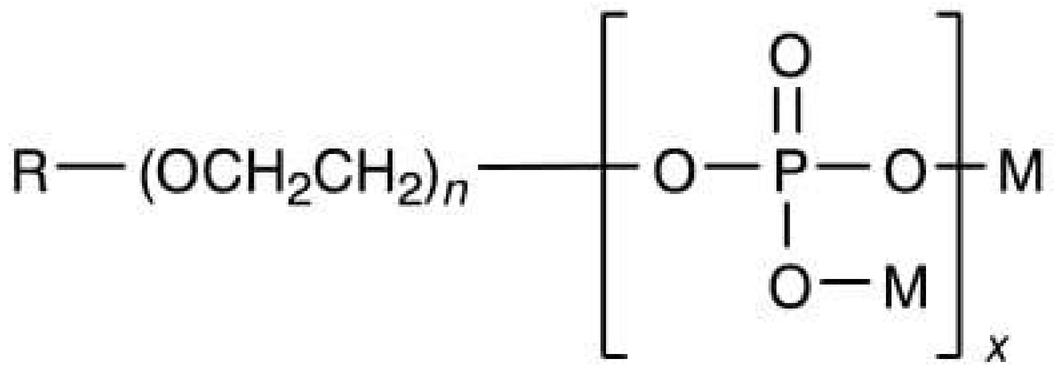
12.26

Surprisingly, other investigators were unable to confirm the adverse effect of nonionic surfactants of low cloud point in the high-temperature dyeing of polyester, even in the presence of electrolytes [111]. This was probably because of the rather low concentrations used. Adducts containing a C_{18}–C_{20} hydrophobe and a decaoxyethylene hydrophile, as well as sorbitan ester ethoxylates were shown to be particularly effective levelling agents. Certain dyes were found to be sensitive to nonionic additives under the stringent conditions of the laboratory dispersion tests carried out in the absence of fibre, but it was pointed out that these systems still performed satisfactorily in actual dyeings [111].

An alternative type of levelling system contains a mixture of ethoxylates with aliphatic esters [112]. This combination exerts a retarding effect on many dyes during heating up to about 100–110 °C, especially if the dyes are present in low concentration. At higher temperatures this retarding effect is increasingly offset by the accelerating effect of the aliphatic esters. This temperature-dependent interaction is said to improve the compatibility of combinations of dyes applied with this system.

The adverse effect of nonionic adducts of low cloud point can be avoided by the use of hybrid agents of the ethoxylated anionic type, variously and confusingly referred to as ‘modified nonionic’, ‘modified anionic’ or ‘weakly anionic’ types. Thus Mortimer [113] has proposed the use of products of the ethoxylated phosphate type (12.27). In this structure, R, as well as the degree of ethoxylation (*n*) may be varied to optimise the overall HLB value. The numerous ether groups are said to enhance the dye-solubilising and levelling capacity, whilst the polyphosphate grouping exerts several useful effects [113]. These compounds:

(1) are sufficiently anionic to avoid most of the disadvantages of conventional nonionic agents with regard to high-temperature instability and the lack of an electrical double layer of value in dispersion stability
(2) behave similarly to more orthodox polyphosphate sequestrants, thus offering some protection from hard water and other trace metal impurities
(3) maintain effective stability in high concentrations of electrolyte
(4) offer possibilities for pH control by varying the nature of M
(5) are fully effective at pH 4–5, the most useful pH range for application of disperse dyes, whereas conventional nonionic types are said to become less effective as levelling agents at pH values less than 7.



$$\mathrm{R{-}(OCH_2CH_2)_n{-}\left[O{-}\overset{\displaystyle O}{\overset{\|}{P}}{-}O\right]_x{-}M}\quad(\text{P bears }\mathrm{O{-}M})$$

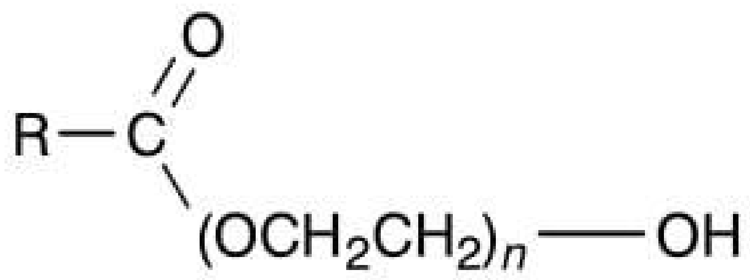
12.27

R = hydrophobe
n = typically 10–20
x = typically 1–3
M = H, alkali metal or organic base

Hence these agents are sophisticated multifunctional auxiliaries, which can take the place of separate additions of levelling agent, sequestering agent and a buffer to control the pH. Nonionic surfactants can be beneficial in minimising the redeposition of the sparingly soluble polyester oligomers that are released from polyester fibres during high-temperature dyeing.

Ethoxylated multi-ester compounds (so-called ‘oligo-soaps’) have been promoted recently as dispersing/levelling agents [114]. These contain a multi-branched hydrophobe with pendant carboxyl groups that are esterified with poly(ethylene glycol). Thus they are similar in structural class to a mono-ester (so-called 'mono-soap') of structure 12.28, a conventional condensate of a fatty acid of high molecular mass with poly(ethylene glycol) but the multi-ester has a much higher relative molecular mass (Table 12.6). A micelle formed from an ethoxylated mono-ester is an aggregate of several molecules, whereas the individual molecule of an ethoxylated multi-ester is said to behave as a micelle, thus exhibiting a much lower critical micelle concentration. The thermal stability of a multi-ester is much greater because this macromolecular structure resists thermal agitation to a much greater degree. This maintains a more stable dye dispersion at high temperature under conditions of high shear. Further advantages include:

(1) solubilisation of the dye takes place at a lower temperature
(2) strike rates at lower temperatures in the dyeing cycle are much slower
(3) solubilisation of oligomer and acrylic size
(4) low foaming.



12.28

R = fatty alkyl group

Table 12.6 Comparison of characteristic properties of mono-ester and multi-ester compounds [114]

	Mono-ester	Multi-ester
Relative molecular mass	Small	Large
Critical micelle concentration	0.400 g/1	0.004 g/1
Foaming tendency	High	Low
Oligomer solubilisation	No	Yes
Size solubilisation	No	Yes

12.6.5 Carriers

Although polyester or cellulose triacetate fibres are normally dyed at high temperatures, their blends with wool are still dyed at or near the boil. In such cases an auxiliary termed a carrier must be used to promote adequate exhaustion of disperse dyes by the ester fibre within a commercial dyeing time. Even in high-temperature dyeing, there are occasions when the usual maximum temperature (around 130 °C for polyester) cannot be used, as when dyeing qualities of texturised polyester that suffer loss of crimp at 130 °C. Carriers are then used to assist more rapid and complete exhaustion, using smaller amounts than at or near the boil. Carriers are sometimes employed to promote migration of unlevel dyeings.

The active component of a carrier formulation is generally a nonionic compound of M_r 150–200 containing a benzenoid ring system. A comprehensive review listed the classes of compounds used together with their general properties, ideal requirements and the mechanisms that have been proposed for carrier action [115]. Carrier compounds fall into four main classes: phenols, primary arylamines, aryl hydrocarbons and aryl esters. Major representatives of these in commercial use include *o*-phenylphenol, biphenyl, methylnaphthalene, trichlorobenzene, methyl cresotinate, methyl salicylate (sometimes mixed with phenyl salicylate), butyl benzoate, ethers of 2,4-dichlorophenol, diethyl or diallyl phthalate and *N*-alkylphthalimide derivatives. Benzaldehyde has been used for the dyeing of aramid fibres [116,117].

Over the last decade the use of carriers has declined markedly and continues to do so, essentially for health, safety and environmental reasons [118–121]. In some countries these products are now virtually banned. Nearly all carrier compounds exhibit all or some of the following: toxicity, physiological irritancy or poor biodegradability (Table 12.7). Typical pollution loads for comparable high-temperature and carrier methods are given in Table 12.8.

Table 12.7 Chemical and biochemical oxygen demand data for various types of carrier chemical [118]

Carrier type	COD (mg/l)	BOD_5 (mg/l)
o-Phenylphenol	1000–2000	200–800
N-Alkylphthalimide	1000–2100	100–200
Arylcarbonate ester	900–1900	700–800
Methyl cresotinate	800–1700	200–800
Dichlorobenzene	500–1000	0
Trichlorobenzene	300–1000	0

Table 12.8 Chemical and biochemical oxygen demand data for high-temperature and carrier dyeing methods [120]

Polyester dyeing method	Liquor ratio	BOD_5 (mg/l)	COD (mg/l)	BOD_5: COD	Harmful factor*
High-temp.	40:1		584		140.2
jet dyeing	40:1	165	722	1:4.4	72.2
Carrier dyeing	40:1	200	2043	1:10.2	408.6
on the winch	20:1	189	1888	1:10	188.8

* Harmful factor = g COD per kg of dyed goods

Harmful effects from carrier dyeing can arise in three ways:

(1) residual carrier in the dyebath contributes to effluent pollution and may be environmentally harmful
(2) carrier that is volatilised during dyeing or subsequent heat setting becomes an atmospheric contaminant
(3) residual carrier in the fibre can be a health hazard, as well as causing an unpleasant odour on heating or during storage.

The degree of carrier action is important in practice and varies considerably. For example, the phthalates have little action on polyester but are efficient on cellulose triacetate, for which they are the most widely used compounds. *Ortho*-phenylphenol and the chlorinated benzenes are generally powerful carriers for polyester, whilst methylnaphthalene and particularly butyl benzoate are less powerful, Although all carriers tend to promote the exhaustion of dyes, some degree of dye-specific behaviour results from the respective hydrophobic/hydrophilic balance of dye and carrier [102,109].

Some carriers, such as *o*-phenylphenol, tend to lower the light fastness of many dyes if carrier residues remain in the dyed fibre; others, such as the chlorobenzenes, have no effect on this property. Similarly, carrier residues differ considerably in odour. A dry heat treatment at 160–180 °C after dyeing, to volatilise the residual carrier, is the best method of minimising problems with light fastness and odour. The steam volatility of a carrier and its toxicity to human and plant life need careful consideration. For example, *o*-phenylphenol has relatively low volatility in steam and traditionally has been used in machines open to the atmosphere. The chlorinated benzenes, on the other hand, are readily steam-volatile and are toxic, so should not be used in machines where volatilised carrier is likely to condense (for example, on a cooler lid) since drops of condensate may cause ‘carrier spots’ if they fall onto the fabric. Biphenyl is relatively non-toxic to river life but is not readily biodegradable; methylnaphthalene, also of low toxicity, is moderately biodegradable, but halogenated benzenes are both toxic and difficult to biodegrade. Some carriers such as chlorinated benzenes and butyl benzoate are relatively efficient in promoting migration; others, such as *o*-phenylphenol, are less so. When dyeing a blend such as polyester/wool it is useful to consider the extent to which the carrier will promote migration of dye to polyester so as to minimise staining of the wool.

All the carrier compounds mentioned above have little or no solubility in cold water. They are therefore used in the form of emulsions, many being marketed as ‘self-emulsifiable’ liquids that form stable emulsions on dilution in the dyebath. The choice of emulsifying system is very important, not only from the viewpoint of emulsifying the active carrier component, but also to ensure stability of the emulsion under dyebath conditions and compatibility with dyes and dispersing agents, as well as efficacy of carrier action. Thus two carriers of identical active components but with different emulsifying systems may well differ appreciably in behaviour. Two typical formulations [122] are given in Table 12.9, both being completely solubilised concentrates that on dilution in the dyebath give stable emulsions of good dyebath compatibility. The weakly anionic ethoxysulphates and ethoxyphosphates are especially useful emulsion bases for carriers. A small amount of a simple organic solvent such as ethanol may also be added to improve stability.

Most commercial carriers are used in the dyebath at concentrations within the range 1–8 g/l depending on active strength of the carrier concentrate, applied depth, liquor ratio and

Table 12.9 Typical examples of carrier emulsions [122]

Formulation 1	Formulation 2
90% Diethyl phthalate	40% Phenyl salicylate
10% Ethoxylated castor oil (40 mol ethylene oxide)	40% Methyl salicylate
	20% Ethoxylated nonylphenol (20 mol ethylene oxide)

other dyeing conditions. Although carriers exhibit dye-specific properties to some extent a particular carrier will generally have an optimal concentration in the dyebath to give maximum dye yield; higher concentrations will tend to solubilise the dye to such an extent that colour yield is depressed.

12.6.6 Aftertreatments and thermomigration

Cellulose acetate and nylon dyed with disperse dyes are usually given a simple rinse with or without a synthetic detergent (anionic or nonionic) after dyeing. Most cellulose triacetate is similarly treated; however, some full depths are given a clearing treatment to remove surface dye so as to improve the fastness properties. Such a clearing treatment is more generally important with polyester dyeings. It most frequently takes the form of a reduction clear using 1–2 g/l sodium dithionite in alkaline solution. For triacetate the preferred alkali is ammonia (1–2 ml/l of s.g. 0.800) at temperatures up to 60 °C. Polyester will tolerate more severe conditions; hence the alkali is usually 1–2 g/l sodium hydroxide used at temperatures up to 70 °C, or even higher in continuous 'short-dwell' processes. This treatment works mostly by reductive fission of azo dyes and by converting anthraquinone dyes to their soluble leuco forms. It is also advantageous to use 1–2 g/l of a nonionic surfactant in the reduction clear to assist solubilisation of the reduction products and in some cases their thorough removal is ensured by a subsequent treatment with a nonionic detergent alone. Fatty acid ethoxylates of the type mentioned earlier (structure 12.26) are excellent nonionic agents for use in reduction clearing.

This process, however, is not only expensive in itself, but creates additional expense through the need to deal with an environmentally unacceptable effluent. There is also the cost and inconvenience in carrying out two changes of pH: first from the acidic dyebath to the alkaline reduction clear, followed by neutralisation of the substrate after the reduction clear. It is not surprising, therefore, that reduction clearing is nowadays avoided as much as possible. One possibility is to use specialised dyes that can be cleared with alkali alone (section 4.9.2): this avoids the environmental nuisance of the reducing agent but still leaves alkali and the need for two pH changes.

Alternative reducing agents are still sometimes proposed and evaluated. A detailed comparison of five reducing agents has been reported: sodium dithionite, thiourea dioxide, iron(II) chloride/gluconic acid, sodium hydroxymethanesulphinate and hydroxyacetone [123]. Results of fastness tests on black polyester dyeings variously aftertreated are given in Table 12.10.

Hydroxyacetone must be used at temperatures above 80 °C on account of its sluggish action. Nevertheless it did not give adequate improvement of fastness to washing. It gives high COD values and has an unpleasant smell. The reducing power of sodium hydroxymethanesulphinate, even with anthraquinone as activator, is insufficient under these conditions. It did not give adequate improvement of washing fastness. Iron(II) chloride has the environmental advantage that it does not contain sulphur but the gluconic acid complexing agent results in relatively high COD values. Improvement of washing fastness was inadequate. Only thiourea dioxide gave results as good as sodium dithionite. It is three times more expensive but causes only half the sulphur pollution of dithionite. The relative usefulness of these two reducing agents really depends on the dyeing process. In the winch, the slow production of active species from thiourea dioxide is a disadvantage when working

Table 12.10 Fastness of black polyester dyeings after various reduction clearing treatments [123]

	Fastness properties		
		Perspiration	
Reduction clear	Washing at 60 °C	Acidic	Alkaline
Untreated control	1–2	2–3	2–3
Hydroxyacetone	2–3	4–5	4–5
Sodium hydroxymethanesulphinate	2–3	4–5	4–5
Same, with anthraquinone activator	3	4–5	4–5
Iron(II) chloride/gluconic acid	3	4–5	4–5
Thiourea dioxide	4–5	4–5	4–5
Sodium dithionite	4–5	4–5	4–5

with the counterflow. On the other hand it could be an advantage in jet dyeing machines, although this only arises if reduction of the dye occurs relatively quickly. In closed machines, sodium dithionite is more effective.

Several reduction clearing auxiliaries have been introduced under commercial brand names, their composition in many cases not being revealed. At least one of these is designed to be used under acidic conditions [124]. Advantages claimed for this product include: no pH changes needed, low COD, high biodegradability, low toxicity, with further savings of time and water consumption. Moreover, since the agent is added directly to the exhaust dyebath any residual dye present is decolorised before discharge to effluent. Although highly effective with the majority of dyes, in a few cases (e.g. CI Disperse Yellow 29, Violet 35 or Blue 56) a higher concentration is needed.

Polyester dyed with disperse dyes generally shows excellent fastness to wet treatments and rubbing after thorough reduction clearing and drying at low temperature (below 120 °C), irrespective of the dyes used. However, cost-effective production and the requirements for fabric dimensional stability demand the use of a combined drying and heat setting treatment at temperatures in the range 150–210 °C, most frequently at 180 °C. This causes some dyes to migrate from the core of the fibre to the surface, thus tending to negate the effect of reduction clearing. This surface dye is a potential source of lower fastness to rubbing and wet treatments [125–127], although the extent to which this occurs depends greatly on the dye and its applied depth. This phenomenon has been termed ‘thermomigration’, its effect on fastness varying considerably because of the generally adverse influence of surfactants, lubricants, softeners, antistats and so on. Similar problems occur on cellulose triacetate. A method for assessing the influence of auxiliaries on thermomigration has been published [128]. This is carried out with 1/1 standard depth CI Disperse Blue 56 (or other suitable dyeings) and the fastness to an ISO C02 washing test is determined after reduction clearing and stentering at specified temperatures. A detergent-based, rather than soap-based, washing test would be more critical [129].

The mechanisms operating during thermomigration in the presence of a surfactant have been evaluated experimentally [130]. The overall mechanism consists of four main processes:

(1) extremely rapid attainment of equilibrium between dye in the surfactant layer and dye in the surface zone of the fibre
(2) rapid diffusion of the dye molecules from the interior of the fibre towards the surface
(3) slower diffusion of surfactant molecules into the substrate phase
(4) eventual formation of a composite dye–fibre–surfactant phase in the surface region.

In fact thermomigration readily takes place in the absence of surfactant, albeit usually to a lesser extent. In this case only the second of the above processes takes place. The term 'surfactant' in this model can be interpreted broadly to include any residual surfactant, reduction clearing assistant or applied finish, such as an antistat, lubricant or softener.

No general correlations exist between the degree of thermomigration and the structure of a dye, its molecular mass, diffusion coefficient or fastness to sublimation. Nevertheless, to a limited extent, in a series of disperse dyes of closely related constitution there does appear to be some relation between the hydrophobic–hydrophilic balance of the dye molecule and its susceptibility to thermomigration. In such restricted series of related dyes, thermomigration decreases with increasing hydrophobicity [130]. This could be related to the strength of dye–fibre hydrophobic bonding, stronger bonding tending to limit migration of dye to the fibre surface. There seems to be a relationship between thermomigration and the degree of interaction between dye and surfactant, more specific interaction leading to greater thermomigration [130]. The degree of interaction in this work was deduced from specific conductivity measurements.

It is important to recognise that the degree of thermomigration in itself is not necessarily indicative of any practical implications that may show up in fastness tests [129]. For example, CI Disperse Blue 60 thermomigrates to an appreciable extent, as measured by solvent extraction of the dyed fibre after stentering. Nevertheless, in most wet fastness tests it still gives excellent results simply because it has relatively low substantivity for adjacent fibres (especially nylon) in wet fastness tests. Conversely, a dye may show very little actual thermomigration yet give poor wet fastness after stentering on account of its high substantivity for nylon under the conditions of test. Direct measurements of dye diffusion behaviour generally have little practical significance in themselves, unless they can be related to the effects on fastness properties. Problems arising from thermomigration are best avoided by selecting dyes that show acceptable washing fastness after heat setting treatment and by ensuring that all surfactants from dyeing and afterclearing are completely rinsed out. Careful choice of finishing agents and finishing conditions is also important.

In heat setting and curing, for example, temperature has a greater effect than time in promoting thermomigration [131]. Thus improved fastness to rubbing and wet treatments may be achieved using a selected durable press/softener finish (incorporating a rapidly reacting resin/catalyst system) giving the required finish effect at 140–160 °C. The longer curing time required at a lower temperature has a less deleterious effect than a higher temperature (such as 180 °C) for a shorter time. Another means of minimising the effects of thermomigration is to apply certain mildly reducing chemicals after dyeing. The application by padding of a polysiloxane and an organotin catalyst along with any other finishing agents [131,132] gives rise to a reducing effect during subsequent dry heat treatment that is capable of decomposing many dyes brought to the surface by thermomigration. Such products do not work successfully with all dyes and finishes, however, and can confer a degree of water repellency that is not always desirable or even acceptable.

The presence in polyester fibres of polymerisation by-products (oligomers) can give rise to problems, particularly if their concentration is greater than normal. With polyesters based on ethylene glycol and terephthalic acid, the amount of oligomer is normally between 1.4 and 1.7%, consisting mainly of the cyclic trimer of ethylene terephthalate with smaller amounts of a pentamer, a dimer containing diethylene glycol residues and traces of other compounds. Significant migration of such oligomers from within the fibre can occur at dyeing temperatures of 110–135 °C, leading to deposits on the fibre and/or machine surfaces and sometimes also to interference with dispersion stability, since dispersed oligomer particles form potential nuclei for the crystallisation and agglomeration of disperse dyes. Discharge of the spent hot dye liquors without prior cooling is the best way of avoiding oligomer problems. Reduction clearing will normally remove any deposits from the fibre surface. Deposits on machine surfaces must be removed by regular cleaning at high temperature with strong solutions (5 g/l) of sodium hydroxide together with thermally stable surfactants and solvents.

12.6.7 Continuous dyeing

The conventional method of continuous dyeing with disperse dyes is the pad–thermofix process [133,134], most frequently used for polyester/cellulosic blends although it can be used with 100% polyester (or cellulose triacetate) materials. The auxiliaries normally used at the padding stage include a thickening agent as migration inhibitor and a wetting agent. Alginates and other polyelectrolytes such as polyacrylamides are popular as migration inhibitors. Anionic sulphosuccinates are suitable wetting agents; since cloud point problems do not arise in continuous dyeing to the same extent as in batchwise processes, nonionic ethoxylates may also be used, often fulfilling a dual role as wetting and levelling agents. An addition of acetic acid to give pH 5–6 is usually adequate when applying disperse dyes alone, although certain processes may demand selection of dyes stable at higher pH, as in the combined alkaline application of disperse and reactive dyes to polyester/cellulosic blends. In some processes, too, the use of hydrotropes such as polyglycols and their esters, as well as of urea and related compounds, can be useful to enhance the degree of fixation.

12.6.8 Printing

Printing with disperse dyes is generally carried out using a thickening agent and an acid donor to maintain a low pH during steam fixation. High-solids thickeners such as crystal gum or British gum give optimal sharpness of outline but suffer from the disadvantage of forming brittle films [29]. Hence low-solids thickeners such as alginates and locust bean ethers, which form more elastic films and are more easily removed in subsequent washing-off, are preferred. Further additions may include a fixation accelerator (hydrotropes such as urea, thiodiethylene glycol, cyclohexanol, dicyanoethylformamide) or a carrier and an oxidising agent, such as sodium chlorate or sodium *m*-nitrobenzenesulphonate, to inhibit the possible reduction of susceptible dyes during steaming. The dispersing agent present in the disperse dye formulation can have an influence on printing problems involving loss of viscosity of the print paste and reduction of some azo dyes. Loss of print paste viscosity is particularly associated with synthetic thickeners. Nonionic formulations of disperse dyes were developed to counteract this problem; in these brands the usual anionic dispersing agent was wholly or substantially replaced by a nonionic system.

Freedom from electrolytes is also desirable for much the same reasons. The nature of the cations associated with the sulphonate groups in lignosulphonate dispersing agents is important, since it affects the hydrophilicity of the agent, this aspect having the primary influence on the absorptive behaviour of the dispersant. The concentration of ionised functions affected by the nature of these cations correlates directly with conductivity, printing paste viscosity and azo dye reduction [91]. A detailed investigation of three inorganic (Na, K, NH_4) and six amine salts of lignosulphonates showed the triethanolamine salt in particular to offer the greatest benefits. The results of these conductivity and print paste viscosity measurements are shown in Table 12.11. Apart from the beneficial effects of the triethanolamine salt on print paste viscosity, this agent showed the least sensitivity to pH, did not promote reduction of azo dyes and was an effective sequestrant for dissolved iron and copper ions.

Table 12.11 Conductivity and print paste viscosity data for various salts of lignosulphonate dispersant [91]

Lignosulphonate cationic salt	Conductance (m.mhos) at 5% dispersant concentration	Print paste* viscosity (cps) at 25 °C
Nonionic control	–	71 000
Conventional low-sulphonated Na salt	9.80	1 800
Low-electrolyte (Na) lignosulphonate	5.26	29 000
Dimethylamine salt	4.75	23 000
Trimethylamine salt	4.34	27 500
Triethanolamine salt	3.31	41 000

* Viscosity sample: 8g dispersant in 970 ml water at pH 7 added to 30 g synthetic thickening

For polyester, the washing-off process to remove unfixed dye and thickening agent is generally a reduction clear as described in section 12.6.6. A simple wash-off with nonionic surfactant must be used on cellulose acetate or triacetate, although a mild reduction clear may be preferable on triacetate.

Discharge effects on acetate are carried out by overprinting dyed grounds with a thickened paste containing the reducing agent thiourea dioxide and thiodiethylene glycol; a disperse dye stable to these reducing conditions may be added to a similar paste to give a contrast illuminated effect. Similar effects may be produced on polyester by printing a discharge (reducing) paste onto fabric that has been padded with dye; reduction of the discharge areas and simultaneous fixation of dye in the undischarged areas then takes place during subsequent steaming. The discharge paste may contain a reducing agent such as zinc formaldehyde-sulphoxylate or tin(II) chloride, although special ranges of alkali-dischargeable dyes are available that require only alkali (section 4.9.2). Reduction-stable dyes may be added to the discharge paste to create illuminated effects. More detailed recipes are available elsewhere.

12.6.9 Stripping

Non-destructive stripping can be carried out at dyeing temperature with surfactants, a nonionic type with a high cloud point being particularly effective. In the case of polyester the stripping effect can be increased markedly by adding a carrier that has migration-promoting properties, the chlorobenzenes and butyl benzoate being particularly effective, although this is now much restricted on health, safety and environmental grounds. The efficiency of destructive stripping depends on the fibre and dye types. The most usual method is to use a reduction process (alkaline sodium dithionite) together with a nonionic surfactant and, where possible, a carrier, the temperature being varied to suit the fibre. In some cases, particularly with anthraquinone dyes, an oxidation treatment (chlorite, hypochlorite or permanganate) may be more efficient. Occasionally a sequential combination of oxidation and reduction treatments may have to be used.

12.7 REACTIVE DYES

12.7.1 Cellulosic fibres

As described in Chapter 7, the various ranges of reactive dyes for cellulosic fibres differ considerably in their reactivity and the number of application procedures is bewilderingly large, including numerous variants within each category of batchwise, continuous, semi-continuous and printing methods. Even a specific method may require modifications to suit a particular quality or form of substrate, dyeing machine or the specific dyes selected from a given range. Fortunately certain general principles are applicable to the great majority, if not all, of these methods. The characteristics of each range of reactive dyes and details of their application methods are fully described elsewhere [30], but in the working situation it is especially important with reactive dyes to consult the dye manufacturer's literature.

Recent years have seen considerable research into the modification of cellulose and reactive dyes, specifically to overcome some of the drawbacks of this dye–fibre system, including the limited degree of fixation in full depths, the need for alkali and relatively high concentrations of electrolyte. This research, which is driven by environmental considerations, was discussed in sections 7.10 and 10.9.1. Thus it need not be considered further here.

Exhaust dyeing

The critical importance of substantivity and its overriding influence on application properties has been described in sections 3.2.1, 3.3.2 and 7.5, as well as elsewhere [30]. The essential auxiliaries used to control reactive dyes in batchwise dyeing are electrolyte and alkali. Secondary auxiliaries may include sequestering agents, mild oxidising agents to prevent reduction of certain sensitive dyes and wetting or levelling agents. The classic procedure for dyeing with reactive dyes involves application under substantially non-reactive conditions by exhaustion with electrolyte at a temperature selected according to the reactivity of the particular dyes used, followed by addition of alkali to enhance absorption and, more particularly, to create the conditions through which the dyes can react covalently with the fibre. In the so-called 'all-in' process electrolyte and alkali are present together throughout to bring about simultaneous sorption and reaction, though this inevitably increases the opportunity for hydrolysis of the dye in the dyebath. Application temperatures vary from room temperature to the boil or even higher.

There is as yet no official method of classifying reactive dyes according to their dyeing properties, unlike the situation with direct or vat dyes. Nevertheless, a promising preliminary scheme has been proposed [135] and it is worthwhile presenting the rationale here, since this scheme has a bearing on the use of auxiliaries insofar as they affect levelling properties.

Group 1 – Alkali-controllable reactive dyes

Dyes that have their optimal fixation temperature between 40 and 60 °C belong to this group. These dyes are characterised by relatively low exhaustion in neutral solution before the addition of alkali. This type of dye has high reactivity and careful addition of alkali must be made in order to obtain level dyeing. For these reasons, the name 'alkali-controllable reactive dyes' has been chosen.

Typical examples of dyes belonging to this group are dichlorotriazine, dichloroquinoxaline, difluoropyrimidine and vinylsulphone dyes.

Group 2 – Salt-controllable reactive dyes

This group includes dyes that have their optimal fixation temperature between 80 and 95 °C. Such dyes show comparatively high exhaustion before fixation so it is important to ensure that dyeings are level. Salt should be added portionwise at specified stages during the exhaustion process, hence they are termed 'salt-controllable reactive dyes'.

Typical examples of dyes belonging to this group are aminochlorotriazine, bis(aminochlorotriazine) and trichloropyrimidine dyes.

Group 3 – Temperature-controllable reactive dyes

This group includes dyes that react with the fibre at 100 °C or above, without alkali present. Dyes in this group have self-levelling properties so there is no need to exercise control by means of dyeing auxiliaries. Good results can be obtained by controlling the rate of temperature rise.

At present only the Kayacelon React (KYK) range of bis(aminonicotinotriazine) dyes represent this group.

Sodium chloride is undoubtedly the most widely used electrolyte, a particular advantage being its ease of dissolution. Certain dyes, such as brilliant blue phthalocyanines and anthraquinones, are susceptible to aggregation and sometimes even precipitation in its presence, however, and in these cases sodium sulphate, which has a lesser aggregating effect, is preferred. The electrolyte should be free from calcium and magnesium salts and from alkali to avoid premature fixation in a two-stage process. The electrolyte functions with reactive dyes in a manner similar to that with direct dyes, but as reactive dyes are more highly sulphonated and hence less substantive than direct dyes, more salt is required to attain equivalent exhaustion. As with direct dyes, the higher the concentration of salt the greater the uptake of dye, provided over-aggregation and precipitation do not occur. The primary objective is to achieve maximal exhaustion over an optimal dyeing period, taking care to ensure level uptake since this is the only phase during which the rapidly diffusing reactive dyes can migrate. Hence electrolyte may be added in portions over the whole dyeing period.

As might be expected with highly soluble dyes, liquor ratio has a pronounced effect on exhaustion and thus on the amount of electrolyte needed, especially with dyes of low substantivity. Decreasing the liquor ratio from 30:1 to 5:1 would justify lowering the electrolyte concentration to one-sixth but in fact even less than this can be used because of the marked effect on exhaustion of the reduction in liquor ratio. There is another important effect of electrolyte: initially the internal pH of the fibre is lower than that of the dyebath, a state that tends to favour hydrolysis of the absorbed dyes; adding electrolyte tends to equalise these pH values, thus protecting against hydrolysis. In general, the longer the liquor ratio, the lower the dye substantivity and the greater the applied depth, then the higher is the concentration of electrolyte required.

Not long ago a rather cavalier attitude existed towards the consumption of electrolyte, based on the prevailing philosophy that 'salt is cheaper than dye' [136]. This outlook led many dyers to use as much as 20–30% more salt than recommended by dye manufacturers (100–150 g/l being not unknown) in an effort to secure maximum exhaustion. A graphic illustration of the total amount of salt used in reactive dyeing worldwide has been provided [137]: this is 1.8 million tons p.a., equating to 80 000 loaded rail wagons that would stretch for 1000 km from Paris to Berlin. This tendency towards excessive salt usage has been turned on its head, on both ecological and economic grounds. Considerable effort is now devoted to defining application conditions whereby the minimal amount of salt can be used, sometimes supported by computer programs supplied by dye manufacturers [136]. The trend towards lower liquor ratios evinced by machinery developments and the increasing use of bifunctional dyes with their higher average levels of fixation have both contributed to lowering of the amounts of salt used. Special ranges of 'low-salt' reactive dyes have been marketed, giving further emphasis to this important and worthwhile trend [137,138]. In spite of these advances, however, it has been suggested [139] that such developments have not proven to be totally satisfactory.

Consequently, investigations were carried out to explore the potential of cationic surfactants, Groups IA, IIA and IIIA chlorides and carboxylate salts as alternatives to conventional electrolytes [139]. Cationic surfactants proved unsuitable as they promoted only surface deposition with low fixation, most of the dye being easily removed by washing. Groups IIA and IIIA chlorides were precipitated as hydroxides under alkaline conditions and were thus also unsuitable, although amongst Group IA salts potassium and caesium chlorides gave increased exhaustion and fixation of CI Reactive Red 180 (12.29) with increasing salt concentration (Figure 12.12). Fixation increased with the atomic size of the cation ($Cs^+ > K^+ > Na^+ > Li^+$) and equivalent fixation was achieved with about 20 g/l less of KC1 and about 40 g/l less of CsCl compared with a conventional concentration of NaCl [139]. Nevertheless, although potassium and caesium chlorides promoted higher exhaustion and fixation, it is difficult to agree that they are viable commercial replacements for sodium chloride. Significant amounts would still be left in the effluent; they will always be more costly and less readily available in commercial quantities, both short- and long-term.

More promising results were observed with potassium salts of di-, tri- and tetra-carboxylic acids (Figures 12.13–12.15). Multicarboxylate salts facilitate much higher levels of dye exhaustion and fixation than sodium chloride, sodium citrate being particularly effective (Figure 12.16). Although sodium citrate is a chelating agent, it does not appear to affect metal-containing reactive dyes under these conditions [139].

Depending on the reactivity of the dyes used and the applied depth, the pH required for reaction with the fibre varies from 8 to 12 and in practice falls mainly between 9 and 11.

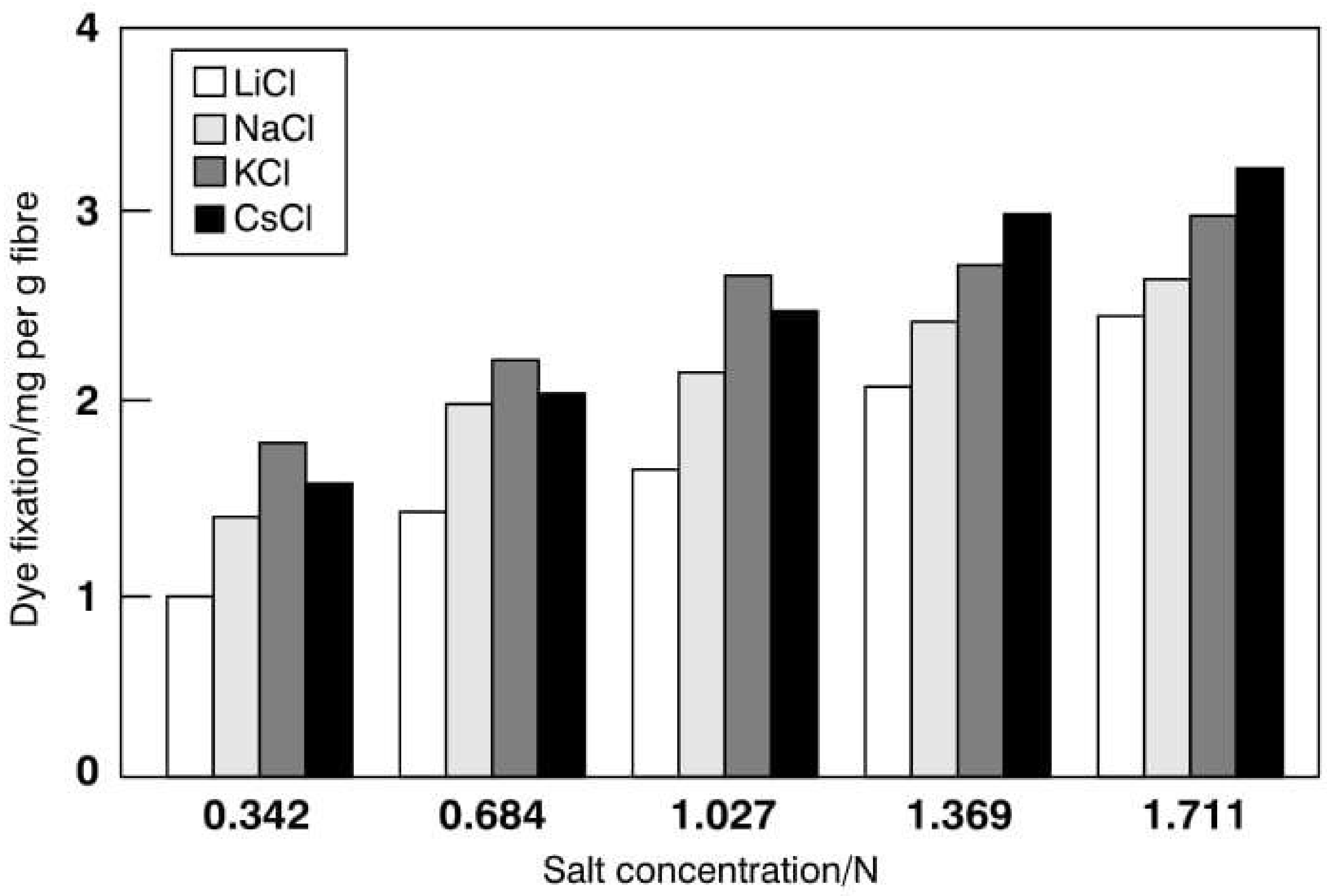
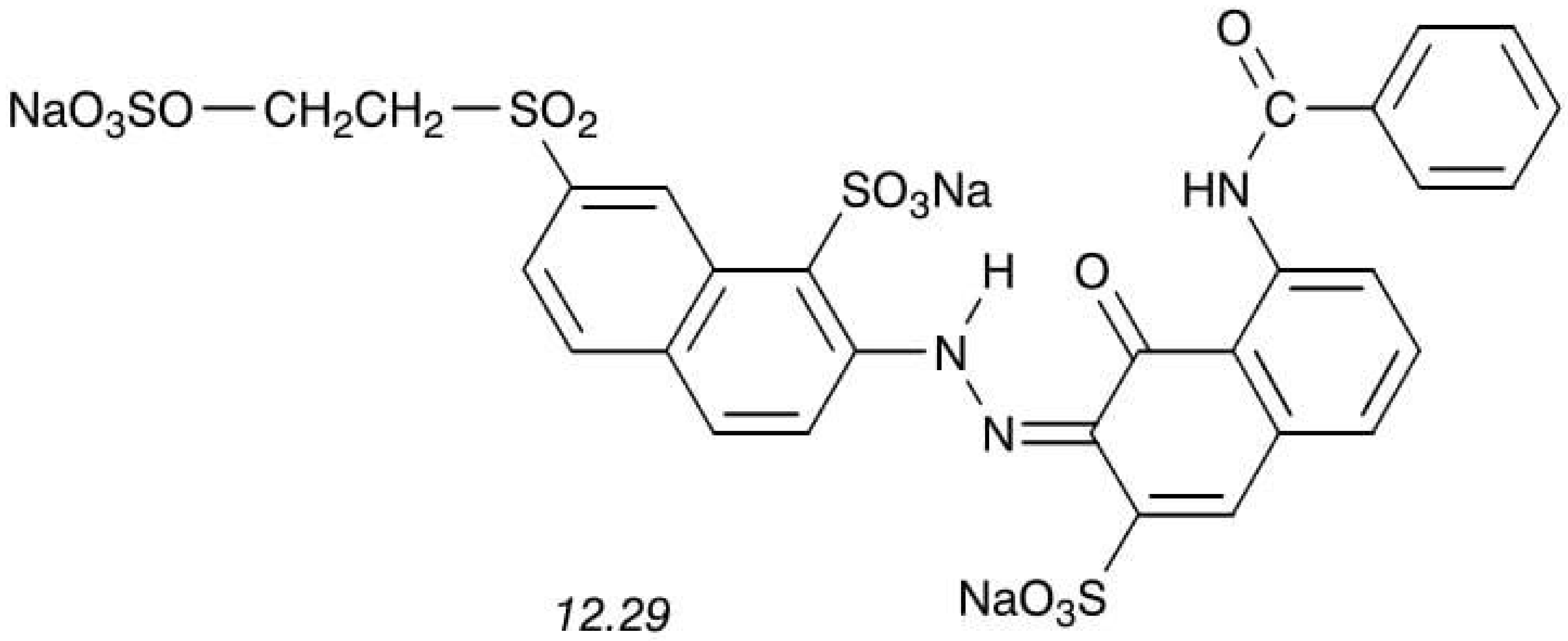
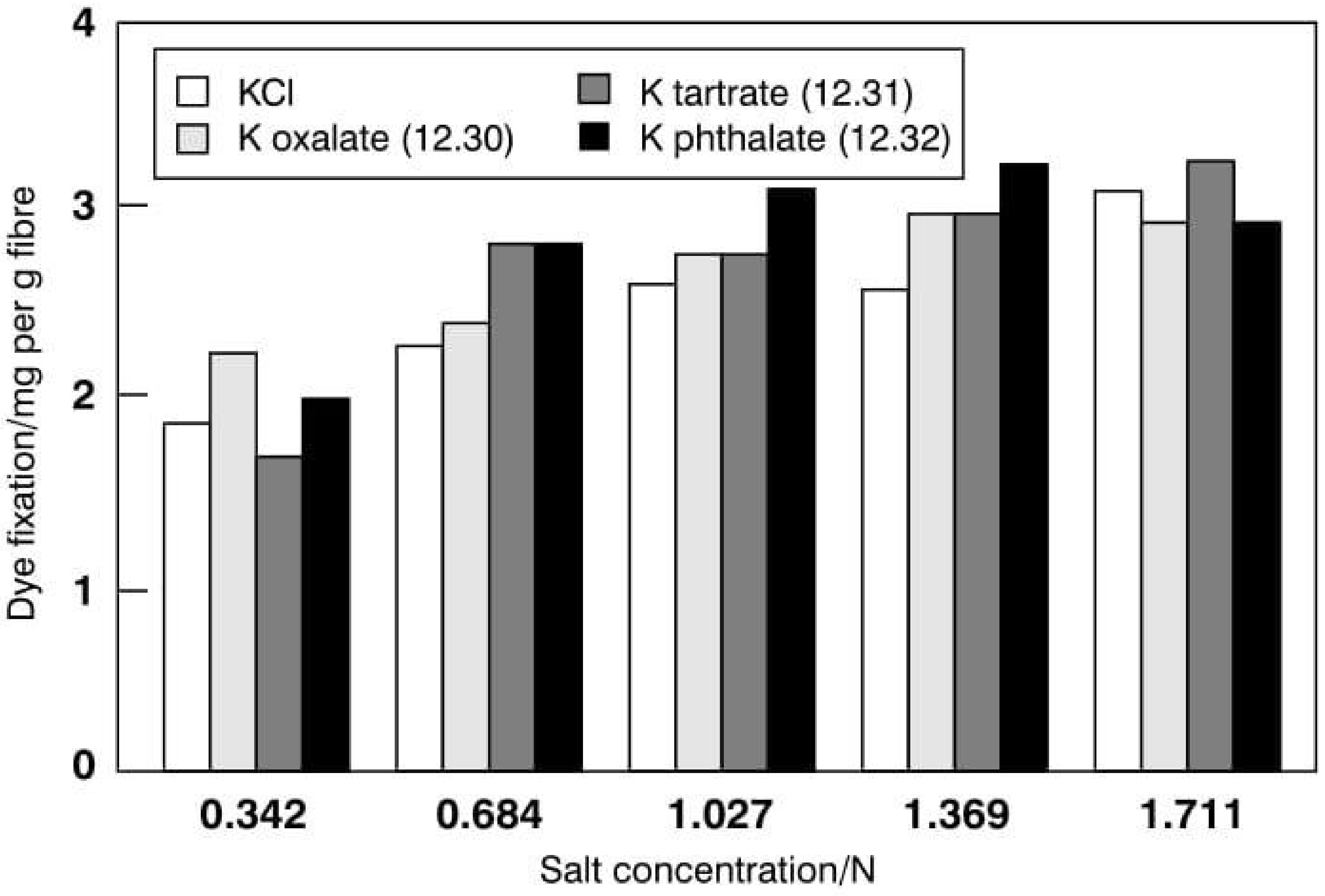


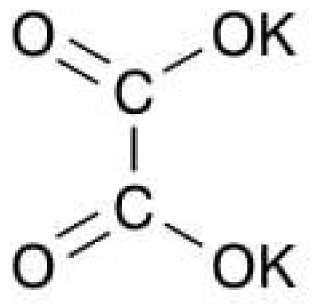
Figure 12.12 Fixation of CI Reactive Red 180 with various concentrations of Group IA chlorides [139]



12.29

CI Reactive Red 180





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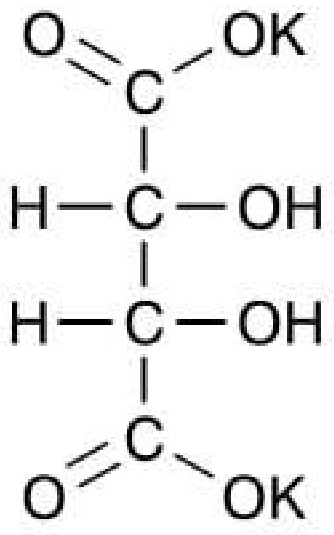

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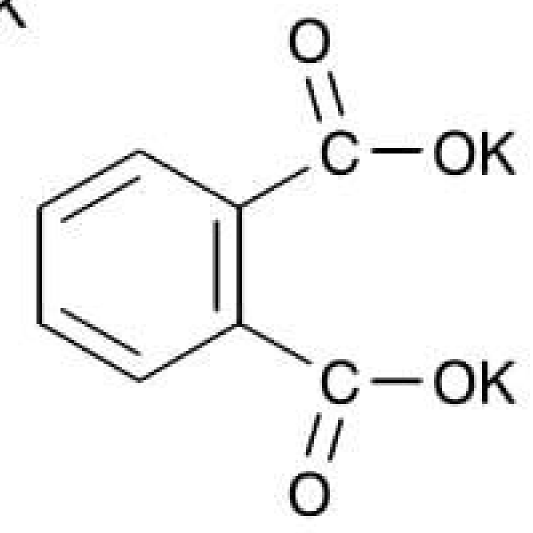

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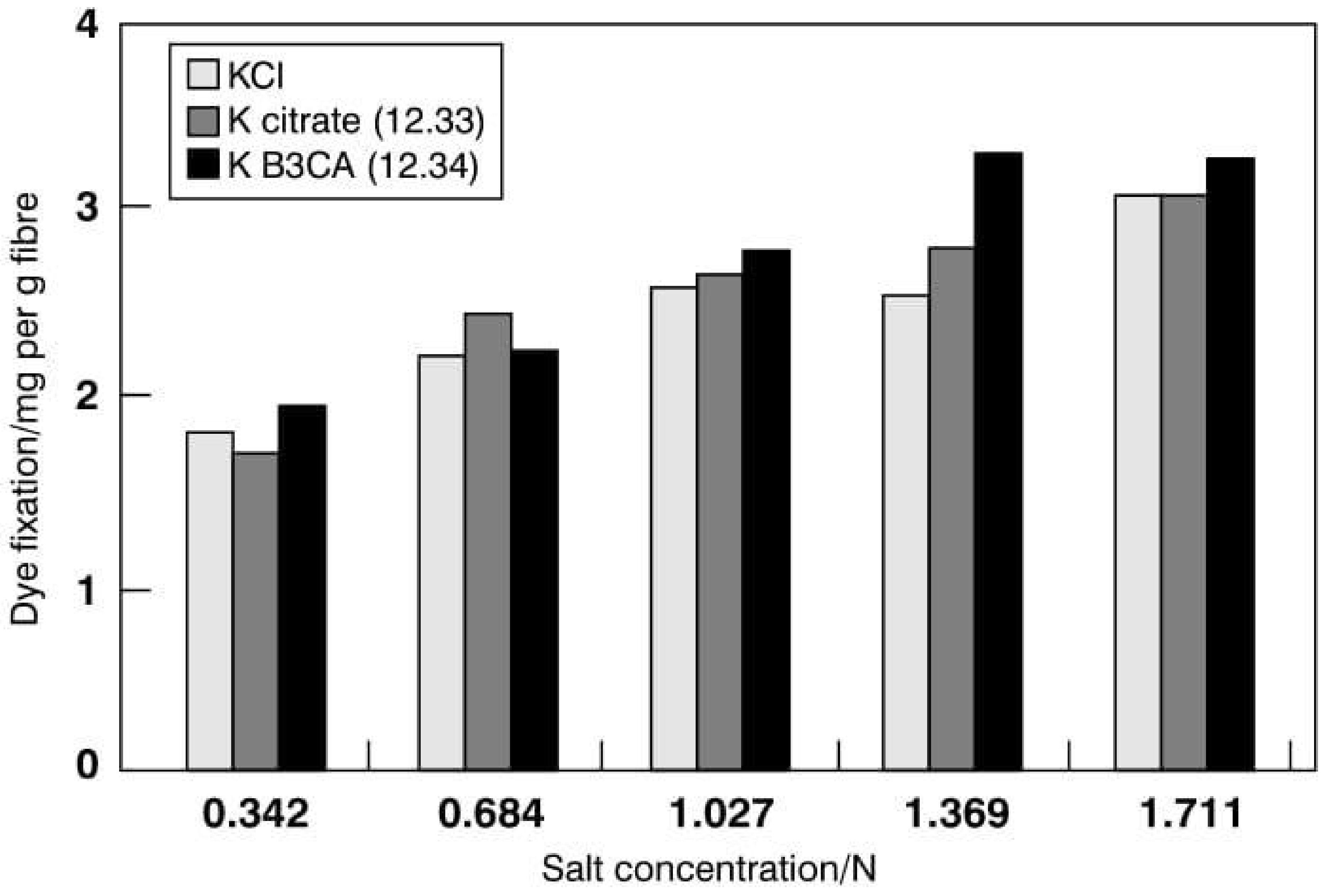
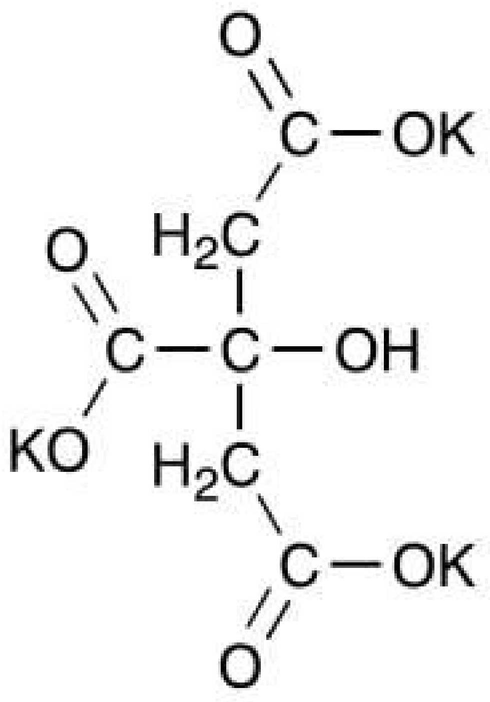
Figure 12.13 Fixation of CI Reactive Red 180 with various concentrations of potassium salts of dicarboxylic acids [139]





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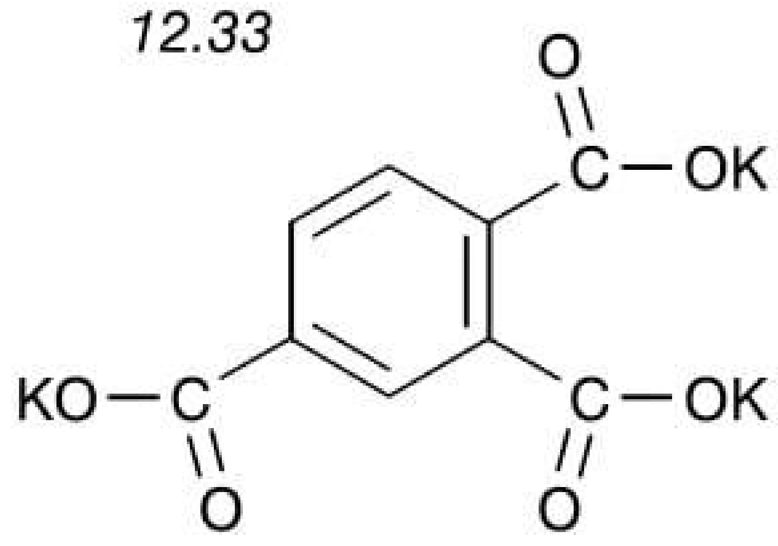

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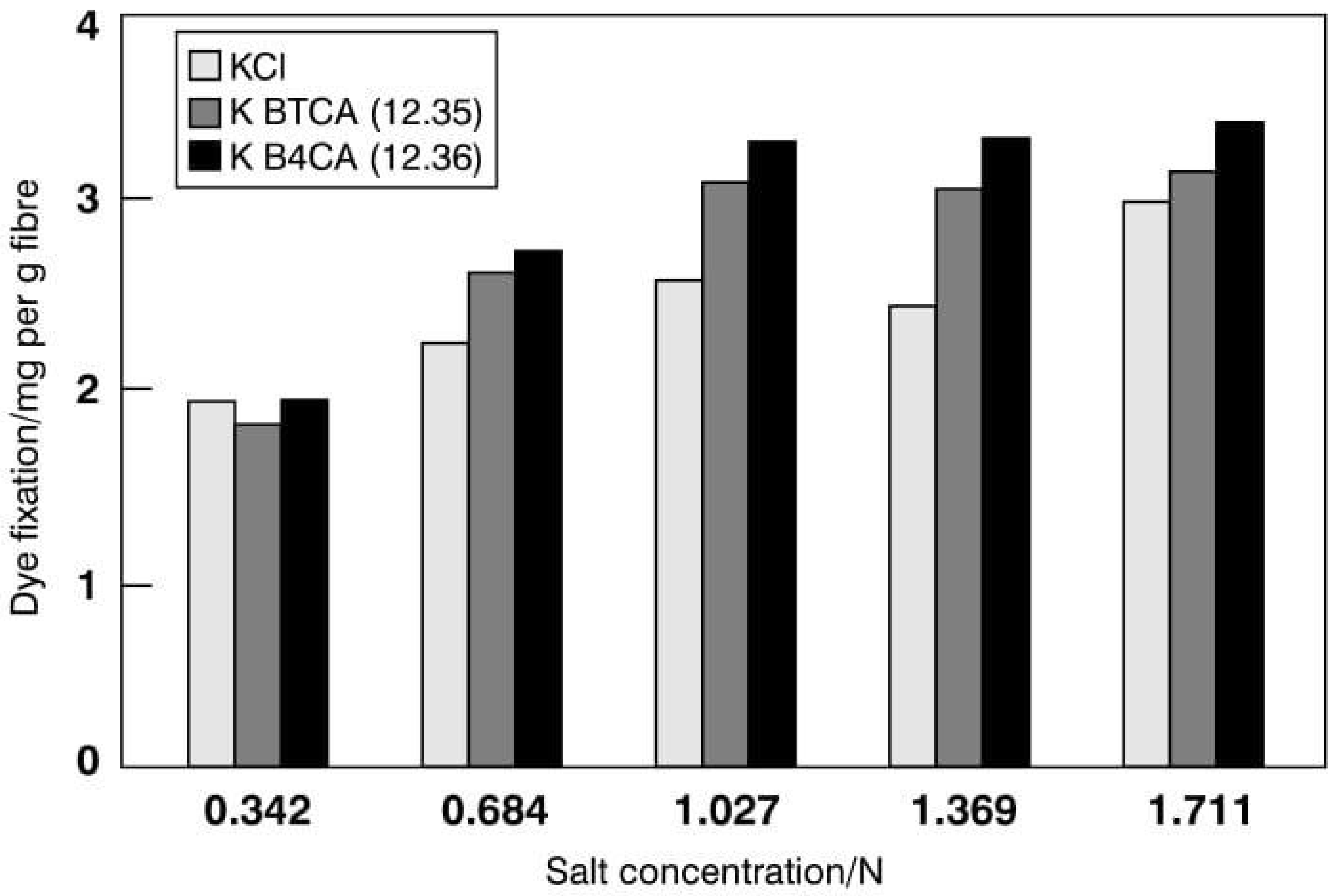
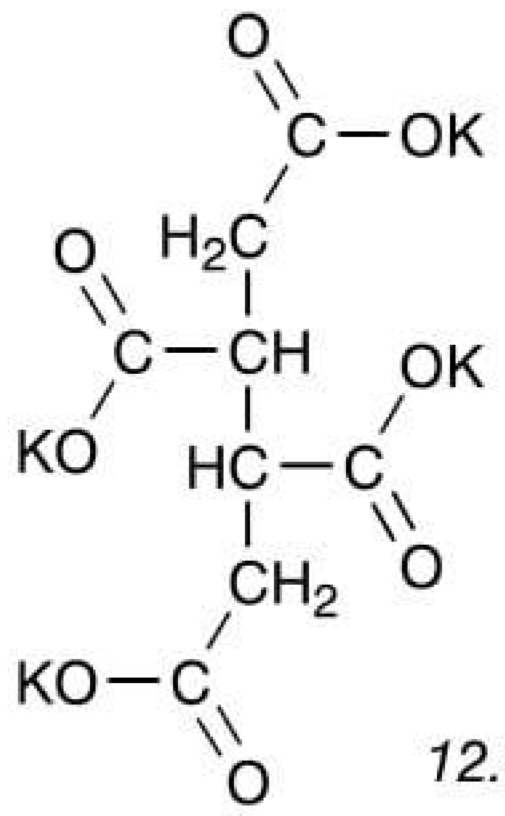
Figure 12.14 Fixation of CI Reactive Red 180 with various concentrations of potassium salts of tricarboxylic acids [139]. K B3CA = Tripotassium benzene-1,2,4-tricarboxylate





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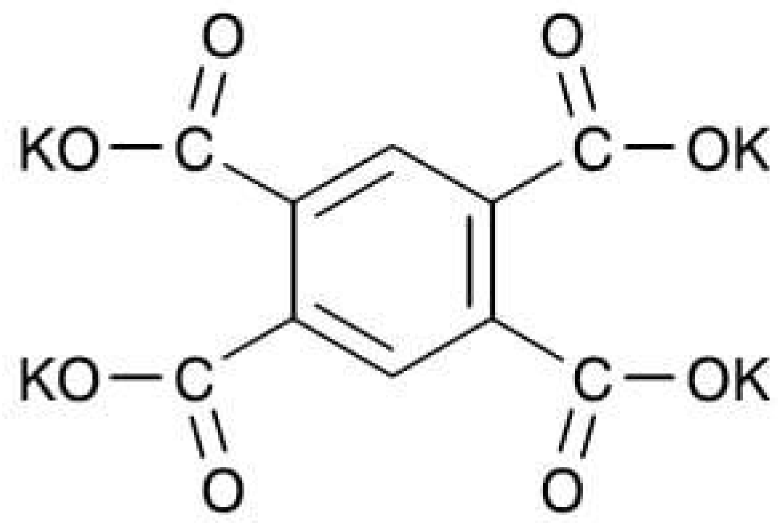


12.36

Figure 12.15 Fixation of CI Reactive Red 180 with various concentrations of potassium salts of tetracarboxylic acids [139]. K BTCA = Tetrapotassium butane-1,2,3,4-tetracarboxylate; K B4CA = Tetrapotassium benzene-1,2,4,5-tetracarboxylate

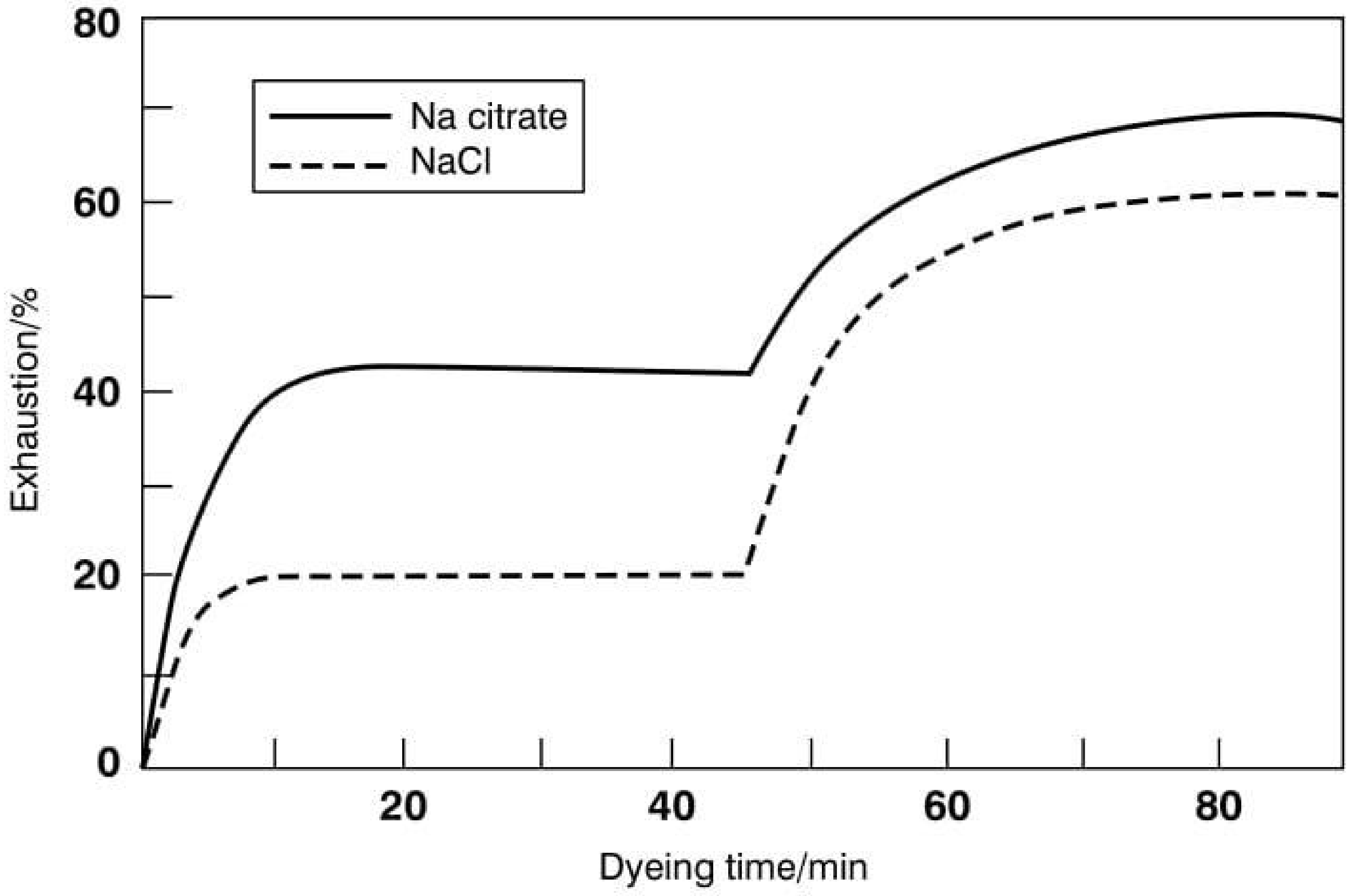


Figure 12.16 Exhaustion profiles for CI Reactive Red 180 in the presence of 1.711N sodium chloride or 1.711N sodium citrate [139]

The most widely used alkali is sodium carbonate, although sodium bicarbonate and sodium hydroxide are also used; these reagents may be used singly or in mixtures. Sodium bicarbonate, for example, can be used as a pH-shift agent, since the pH slowly increases on heating as sodium carbonate is formed (Scheme 12.4). The alkali induces ionisation of the cellulosic hydroxy groups, enabling the dye to react with these nucleophilic anionic sites to form covalent bonds with the fibre (section 7.3.1). It might be thought that increasing quantities of alkali would favour maximal reaction between dye and fibre, but in practice an optimum level of alkali, rather than a maximum, has to be sought. This is because the cellulosate anion tends to repel the reactive dye anion, thus decreasing the efficiency of dye uptake and so increasing the tendency towards hydrolysis of the dye. Consequently, the aim must be to keep the pH as low as possible consistent with maintaining complete reaction within a commercially acceptable dyeing time; however, fixation conditions vary widely according to the dye type and process used.

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

Scheme 12.4

In certain applications sodium silicate is preferred. Replacing sodium carbonate by sodium silicate can increase yields by 10–30%, as well as giving an improvement in fastness to washing. The increase in yield was higher with cold-dyeing than with hot-dyeing types. Cost savings were estimated at 15–35%, or 50–70% in some cases [140]. Occasionally, however, the lower alkalinity of silicate could result in greater hydrolysis with corresponding reduction in yield.

It is opportune at this point to illustrate the combined effects of electrolyte and alkali (Figure 12.17). The initial stage with electrolyte alone at neutral pH approaches equilibrium primary exhaustion of dye; there is no fixation during this stage. Once the alkali is added (in this case after 20 minutes), fixation of the dye begins to take place; at the same time, the alkali contributes to further exhaustion, which is termed secondary exhaustion. The difference between equilibrium exhaustion and fixation at the end of the process represents unfixed dye that requires washing off in order to maximise fastness properties. The profiles of these curves differ according to how the individual dyes respond to the conditions (type and concentration of auxiliaries, pH, temperature). Once the dye is fixed, it cannot migrate. Hence the difference between the exhaustion and fixation curves represents the potential for levelling during the alkaline treatment.

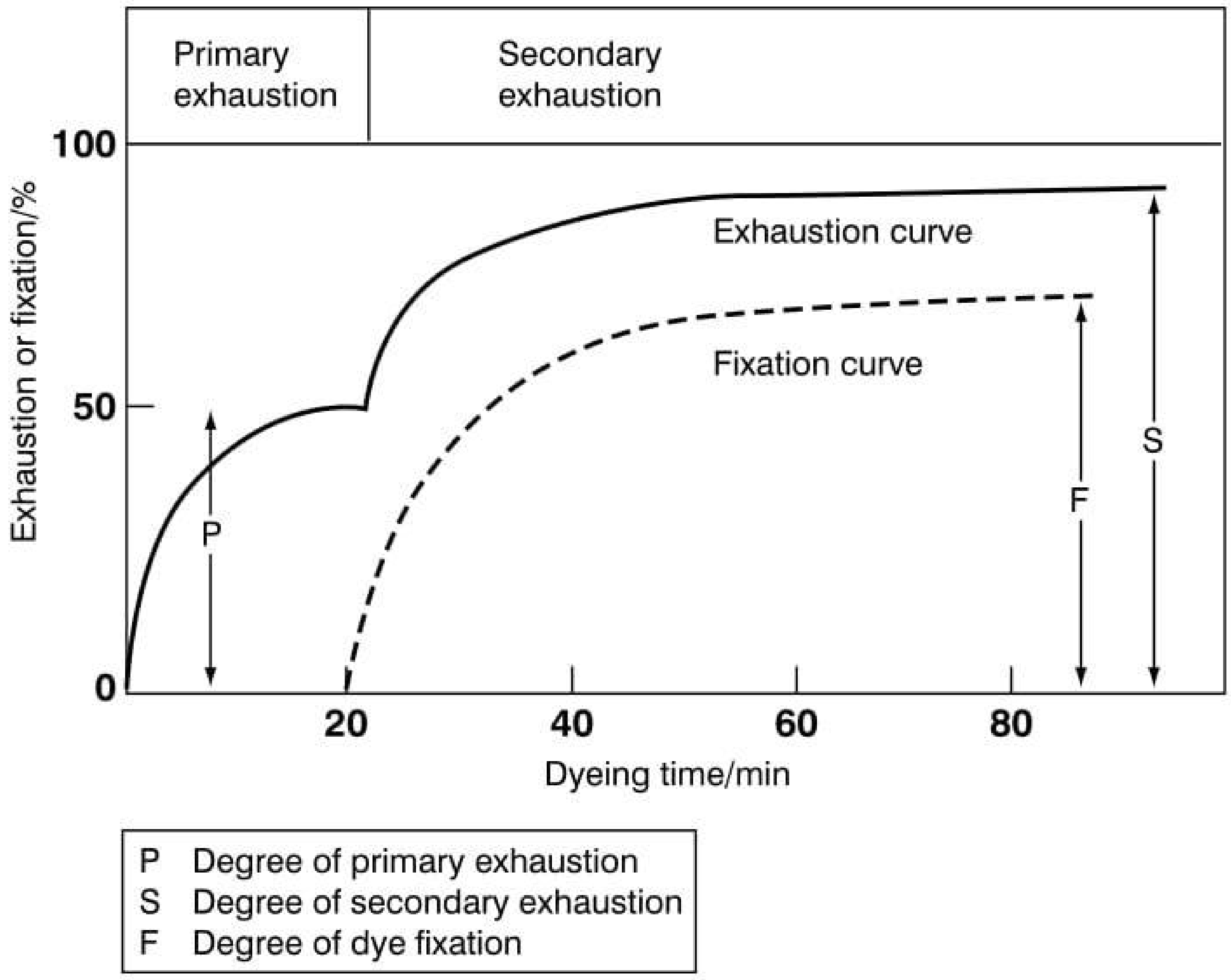


Figure 12.17 Dye exhaustion and fixation profiles in exhaust dyeing with a typical reactive dye [141]

The traditional requirement for alkalinity can be a disadvantage on both environmental and cost grounds. Furthermore, this treatment is not fully compatible with dyeing requirements for other fibres used in blends with cellulosic fibres, particularly polyester, thus complicating the dyeing of such blends. This has favoured the development of so-called 'neutral-dyeing' reactive dyes. These do not require the addition of alkali for fixation but still need electrolyte for exhaustion [142–144]. With these dyes reaction does not occur at neutral pH below 100 °C but fixation becomes optimum at 120–130 °C and pH 6.5–7.5. A pH of 8 is recommended for the hank dyeing of yarn and jig dyeing of fabrics, where dyeing at high temperature is not feasible. This range of dyes is the only one to fall into Group 3 of the classification mentioned previously; hence their levelling is controlled by temperature rather than by additions of alkali or electrolyte.

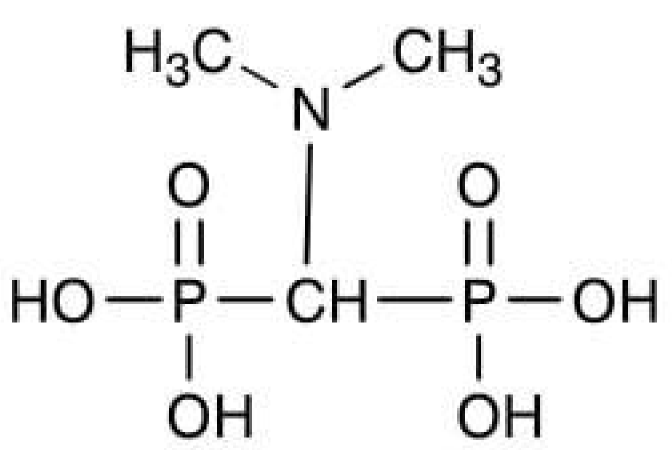
As mentioned at the beginning of this section, the so-called 'all-in' method may be adopted, treatment time being saved by adding the electrolyte and alkali together, albeit at the expense of lower fixation and (usually) inferior reproducibility. Studies of dichlorotriazine dyes applied with various alkalis or combinations of alkalis ($NaHCO_3$, Na_2CO_3/NaOH or Na_2CO_3/$NaHCO_3$) have shown recently that this process can be optimised to give enhanced dye fixation by buffering to give pH 8 or 9 [145].

Reactive dyes in general are not unusually sensitive to hard water. Nevertheless, the alkali used in most reactive dyeing processes may precipitate calcium or magnesium hydroxide on the substrate, to cause problems in later processes. Ideally, soft water with a pH not greater than 7 is preferred. Where the use of hard water is unavoidable, a sodium hexametaphosphate sequestering agent may be used in the minimal amount needed to overcome the hardness, since excessive quantities may bring about a significant reduction in dye yield. Organic sequestering agents of the EDTA type (section 10.2.1) are generally best avoided because they often result in colour changes and reduced light fastness, although they can occasionally be used successfully in minimal quantities [30]. It has been shown, at least with some reactive dyes, that hue changes due to traces of iron or copper in modal fibres (Table 12.12) can be prevented by the use of dimethylaminomethane-1,1-diphosphonate (12.37), 1-hydroxyethane-1,1-diphosphonate (12.38), EDTA (12.39) or certain water-soluble polymers as sequestering agents [146]. However, as discussed later, the potential for trace metals to cause problems at the washing-off stage should not be overlooked [30].

As mentioned previously, once reactive dyes have reacted with the fibre no levelling is possible; hence all levelling must be achieved before the reaction has reached equilibrium. The preferred means is by controlled additions of alkali (Group 1) and electrolyte (Group 2) rather than by using a surfactant-type levelling agent. The latter causes restraining, although such products may be added in minimal amounts to aid wetting and to safeguard against rope marks through lubricating action [30]. A particularly detailed study of the effects of a range of nonionic aromatic and aliphatic ethoxylates confirmed the negative influence of these agents on the fixation of reactive dyes [147–149]. Figure 12.18 shows typical results

Table 12.12 Metal content of regenerated cellulosic fibres [146]

	Metal content (ppm)		
Metal	Modal fibre	Schwarza modal fabric	Lenzing modal fabric
Copper	4.1	6.6	2.0
Iron	46.0	63.0	13.0
Zinc	15.0	20.0	38.0
Magnesium	–	22.0	9.0
Lead	27.0	15.0	<0.1
Manganese	2.2	1.5	0.2
Ash content (%)	0.27	0.37	0.25



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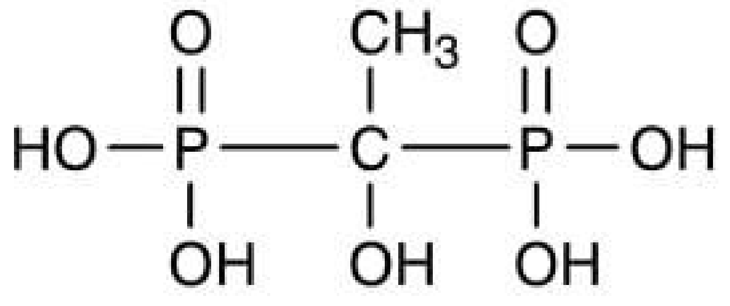
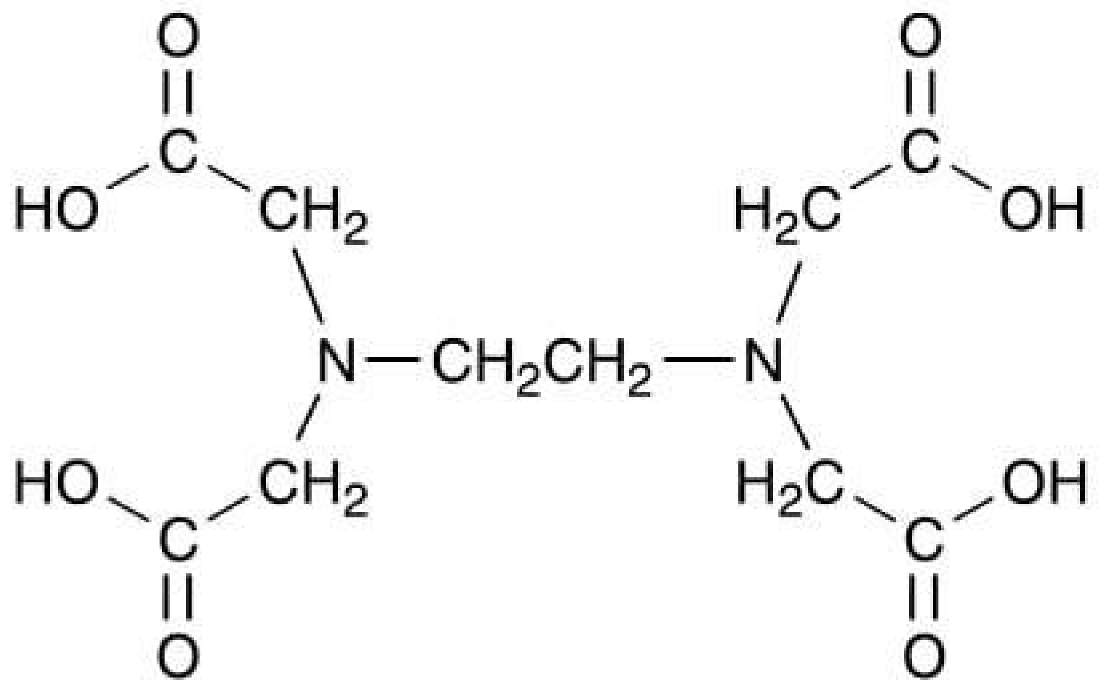


12.38

HEDP



12.39

EDTA

obtained with a nonylphenol ethoxylate (20 mols ethylene oxide) in dyeings of CI Reactive Red 2 (12.40).

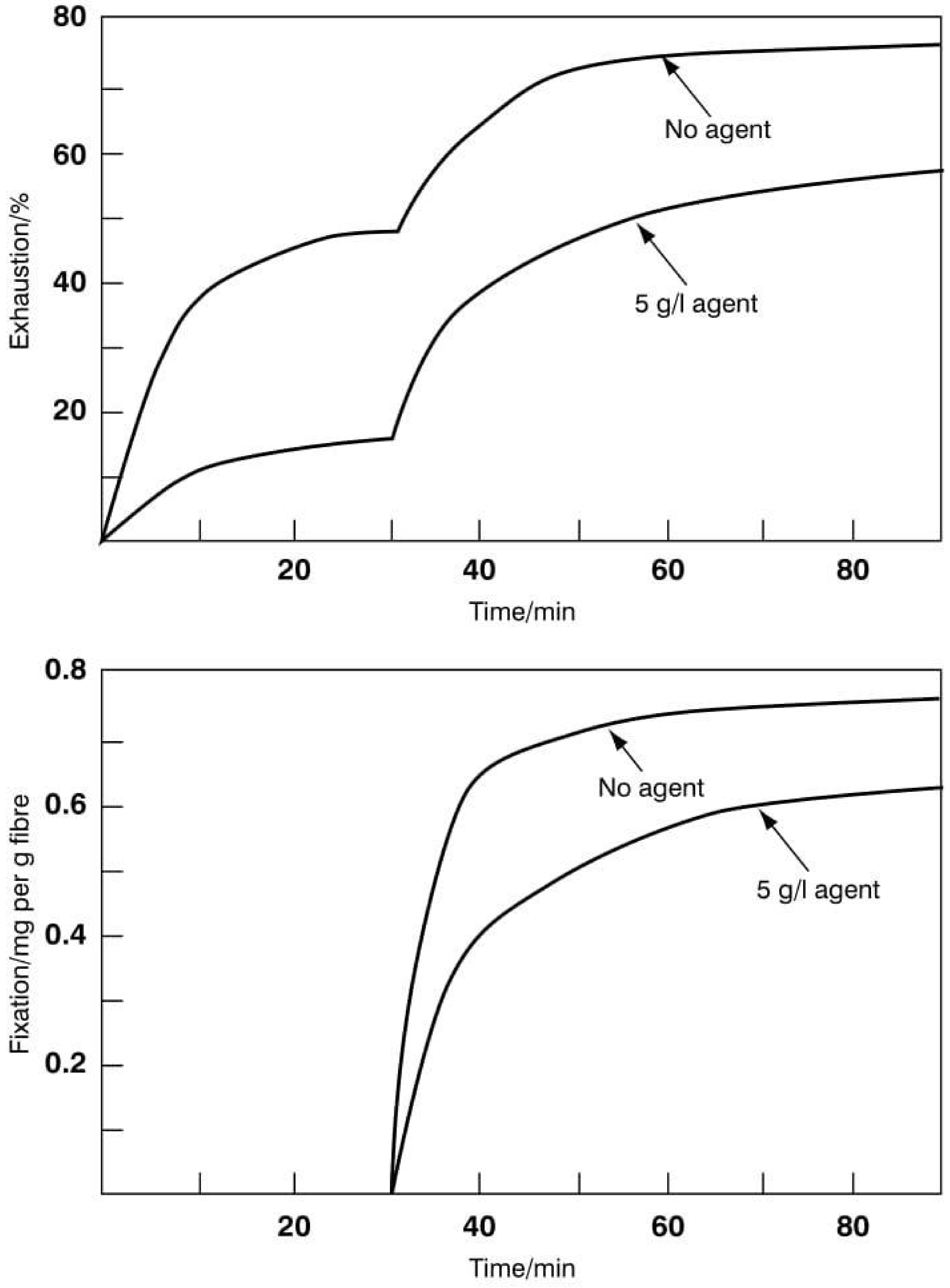
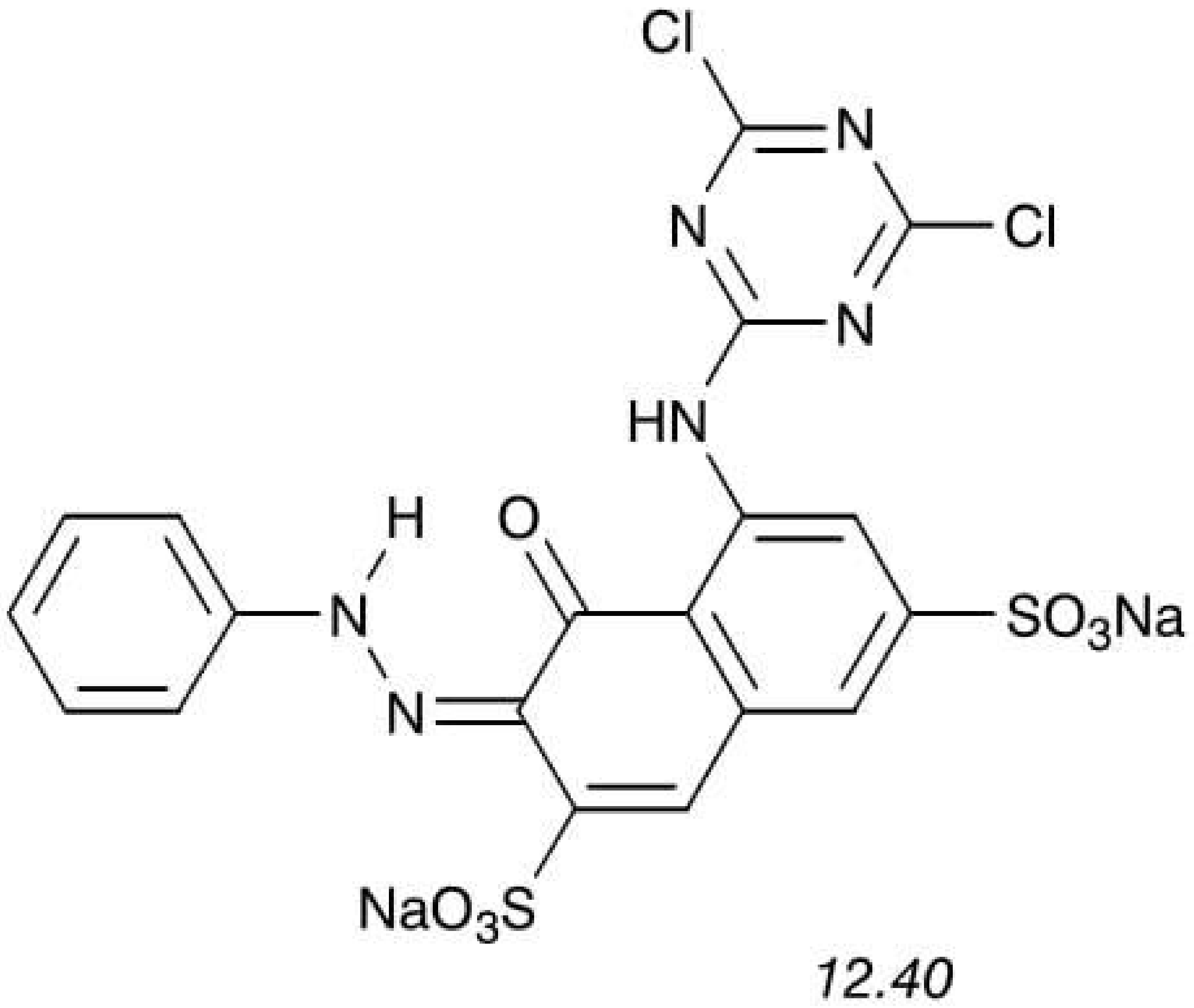


Figure 12.18 Exhaustion and fixation curves for CI Reactive Red 2 in the presence and absence of a nonionic surfactant at 30 °C [147]



12.40

CI Reactive Red 2

However, the decrease in yield varied considerably with dye and surfactant. The magnitude of the effect increased with increasing degree of ethoxylation of the surfactant and varied considerably from dye to dye. Interestingly, this loss of yield occurred even though kinetic evidence indicated that the presence of the nonionic agent decelerated the rate of dye hydrolysis [149]. Spectrophotometric studies [148] showed positive evidence of interaction between the dye and surfactant. This interaction shifts the equilibrium between adsorbed dye and dissolved dye in favour of the dyebath [147]. Electrolyte and temperature also influenced the interaction [148]; higher temperatures tended to destabilise the dye–dye and dye–surfactant interactions, although these interactive effects were partially maintained at normal dyeing temperatures. Thus the possibility of using surfactants as levelling agents for reactive dyeing is best avoided. Similarly, any surfactants added during preparation should be completely rinsed out before dyeing. Provided goods have been prepared thoroughly, it should be unnecessary to add wetting or levelling agents to the dyebath [30]. Mention of the importance of thorough rinsing after preparation applies not only to the need to remove surfactants but also to prevent the considerable number of dyeing faults resulting from residual unevenly distributed alkali and residual peroxide [150].

Various attempts have been made to optimise the exhaust dyeing of reactive dyes. For example, some methods depend on pH control via precisely metered alkali dosing systems [151,152]. The curves in Figure 12.19 show how the fixation rate can be modified considerably by dye-specific alkali metering in order to increase the scope for levelling. Detailed attention to the precise effects of all dyeing parameters with a view to ultimate dye-specific control enables the minimal amounts of auxiliaries to be used that will give safe and effective control. Further advantages claimed include reduced water, steam and energy consumption together with substrate quality improvements [151–153].

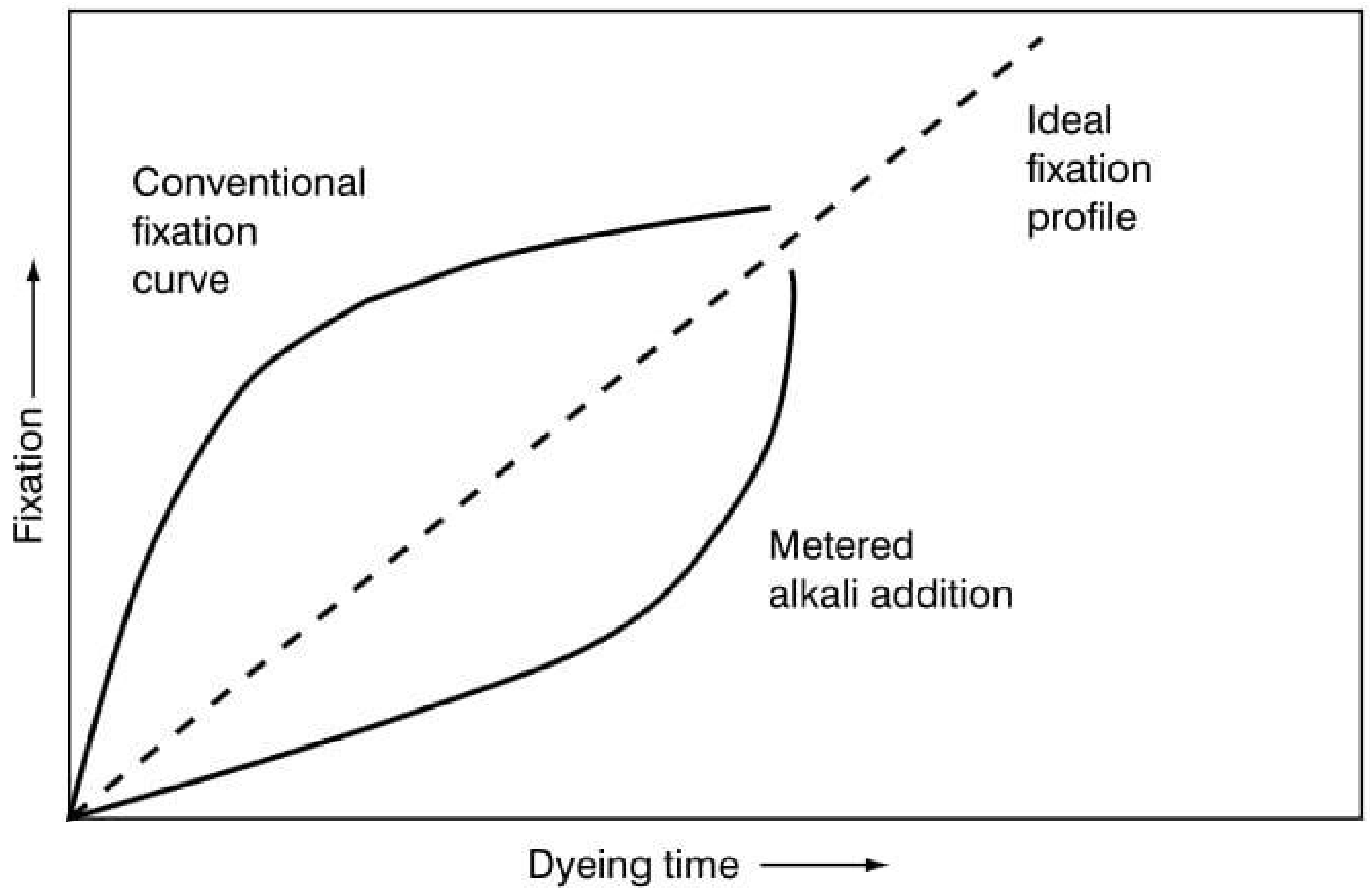


Figure 12.19 Control of reactive dye fixation rate by Remazol automet (DyStar) alkali addition [151]

Neps in cotton fabrics can pose a problem for reactive dyeing. Effective coverage of such dead or immature cotton can be achieved by pretreatment with poly(ethylene imine) on the jig at 10:1 liquor ratio before the dyeing process. The cationic polymer not only gave good coverage of the neps but also improved the colour yield generally. In addition, wet fastness could be improved by a low-temperature curing treatment with a cationic polymer emulsion [154].

Viscose fibres are particularly suitable for dyeing with reactive dyes, the differences in colour yield between dyed viscose and cotton varying between individual dyes and depending on the chromogen present [155]. Salt and alkali requirements are generally lower on viscose than on cotton, although most turquoise and green hues based on phthalocyanines are applied according to special recommendations [30]. A comparison of three types of reactive dye applied to cotton, viscose and lyocell showed little difference in colour between these fibres [156]. The colour strength was lowest on cotton, slightly higher on lyocell and marginally the highest on viscose. It should be borne in mind that the quality of today's viscose is somewhat different from that produced in the 1970s: as regards response to preparation and dyeing parameters modern viscose is generally superior [157]. Hence some care is needed in relating current data to earlier results and many of the older recommendations should not be followed today. Certain dyes are susceptible to reduction, particularly under anaerobic dyeing conditions. An addition of 1–2 g/l sodium *m*-nitrobenzenesulphonate is a useful palliative.

Continuous and semi-continuous dyeing

There are numerous variations of procedure for the continuous or semi-continuous dyeing of cellulosic fabrics with reactive dyes, viable reasons being evinced for the promotion of most of the major ranges of reactive dyes. We are concerned here only with rationale in the selection of auxiliaries; details of the many processing routes can be found elsewhere [30,158–163]. Low substantivity at the padding stage is often preferred in order to minimise tailing, but in fact dyes covering the whole range of reactivities can be used. Highly reactive dyes can be fixed in shorter times at lower pH and are often easier to wash off, whilst those of low reactivity offer greater stability in the pad liquor. The bifunctional types give highly efficient fixation and excellent fastness performance [30].

Many processes require only dye and alkali; for example, on cotton equal concentrations of dye and alkali over the range 5–30 g/l may be used with a pick-up of 60–80%, whilst on viscose the pick-up is usually higher (90–100%) and the alkali reduced to half the quantity of dye. With some aminochlorotriazine dyes both salt and alkali are used – perhaps up to 30 g/l sodium chloride and 10–15 g/l alkali. In some processes sodium silicate is preferred as the main alkali, in order to alleviate the problem of white selvedges. This fault can occur with sodium hydroxide, caused by neutralisation of the sodium hydroxide by carbon dioxide or other acidic atmospheric agents. A wetting agent is generally required in continuous processes to aid rapid wetting at the padding stage. A hydrotrope such as urea may be added, particularly for deep shades, to boost the solubility of less sulphonated dyes and to aid fixation through the mechanism of retaining moisture by hydrogen bonding, particularly in fully continuous thermofixation techniques. If a thickening agent is needed to minimise migration, sodium alginate is preferred since it does not interact with reactive dyes; electrolyte addition may serve the same purpose. An advantage of fully continuous procedures is that minimal quantities of alkali and water are consumed. Two-stage continuous processes, comprising two wet-on-wet paddings with the second pad applying the alkali, are applicable in certain circumstances.

The paramount importance of efficient preparation in producing goods of thorough and uniform absorbency for continuous dyeing cannot be over-emphasised [157,158]; all continuous dyeing systems are heavily dependent on this prerequisite. Typical build-up curves on mercerised and unmercerised cotton fabrics in Figure 12.20 illustrate the significantly higher colour yields attained in a two-bath pad–steam process using sodium silicate (variant B) with vinylsulphone dyes. Recommended variant A and B chemical pad formulations are shown in Tables 12.13 and 12.14, for a steaming treatment of 30–60 seconds at 102–105 °C. In this process, important factors for the control of dye migration include the lowest possible pick-up of dye liquor in padding, minimum addition of wetting agent, sufficient electrolyte in the chemical pad liquor and selection of vinylsulphone dyes of high substantivity. If a one-bath, pad–steam process is used, the recommended variant A and B chemical formulations are as presented in Tables 12.15 and 12.16 respectively. Steaming treatment is again 30–60 seconds at 102–105 °C.

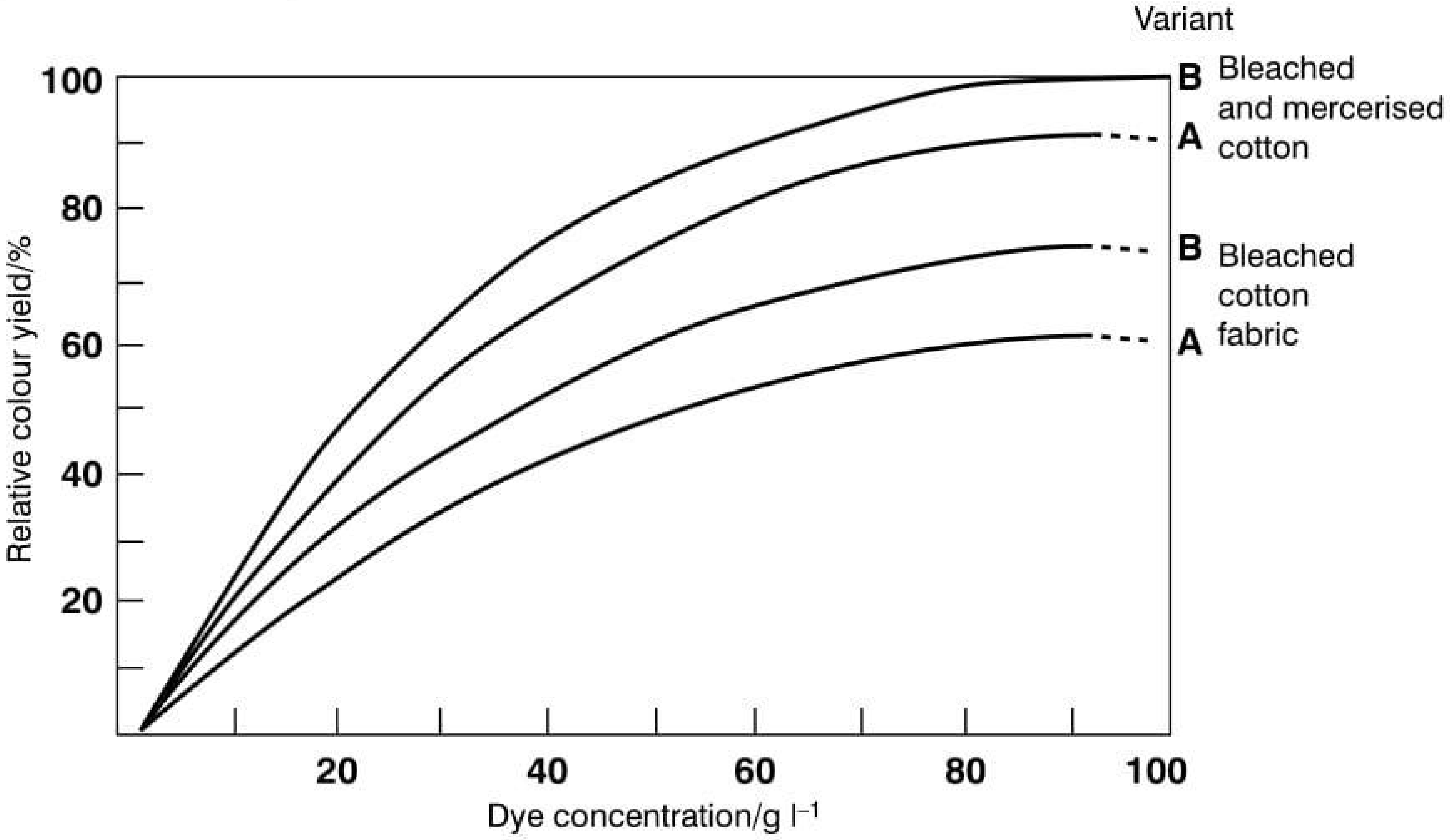


Figure 12.20 Typical dye build-up curves for pad–steam process variants A and B on mercerised and unmercerised cotton [158]

Table 12.13 Chemical pad additions for two-bath salt variant A[158]

Dye concentration (g/l)	<20		20–40		>40	
Steaming time (s)	30	60	30	60	30	60
Sodium chloride or sulphate (g/l)	250	250	250	250	250	250
Sodium carbonate (g/l)	20	20	20	20	20	20
Caustic soda 32.5% (ml/l)	10	5	15	7.5	20	10

Table 12.14 Chemical pad additions for two-bath silicate variant B [158]

Silicate strength (°Be)	Mass ratio $Na_2O:SiO_2$	Silicate addition (ml/l)	Caustic soda solution 32.5% (ml/l)
37–40	1:3.3	900	100
40–42	1:3.3	760	100

Table 12.15 Chemical formulation for one-bath salt variant A[158]

30 g/l	Sodium chloride or sulphate
20 g/l	Sodium carbonate
5 ml/l	Caustic soda 38°Be if <15 g/l Dye
10 ml/l	Caustic soda 38°Be if >15 g/l Dye

Table 12.16 Chemical formulation for one-bath silicate variant B[158]

95 ml/l	Sodium silicate 37–40°Be
8 ml/l	Caustic soda 38°Be (32.5%) if <15 g/l dye
15 ml/l	Caustic soda 38°Be (32.5%) if >15 g/l dye

For the pad–batch fixation of heterobifunctional Cibacron C (Ciba) dyes four alkali variants have been suggested [159]:

(1) Rapid fixation in 5–8 hours using a mixture of sodium hydroxide and sodium silicate, a metering pump being necessary. A high concentration of alkali gives rapid fixation but still allows excellent bath stability at temperatures up to 30 °C.

(2) Fixation in 6–12 hours with a mixture of sodium hydroxide and trisodium orthophosphate, a metering device being necessary. This method is recommended for regenerated cellulosic fibres. This formulation contains the same total amount of alkali as method (1) with the same bath stability, but may be preferred where some buffering capacity is required and sodium silicate is undesirable.

(3) A different combination of sodium hydroxide (reduced amount) and sodium silicate, a metering pump not being necessary. This method demands a longer fixation time (12–24 hours). Bath stability is greater than two hours but the total amount of alkali is inadequate for application to grey goods, where the raw cotton consumes a great deal of alkali.

(4) A mixture of sodium hydroxide and sodium carbonate, a metering pump being necessary. This method avoids the use of either silicate or phosphate and is popular for woven goods and in circumstances where silicate would pose problems. Ideally the carbonate should be free from bicarbonate. This system has less buffering capacity and gives slightly lower bath stability than methods (1) and (2).

Methods (1) and (2) are the most widely used because they offer the most reliable results in bulk-scale processing.

In pad–batch dyeing with the highly reactive chlorodifluoropyrimidine Drimarene R or K (Clariant) brands, it is equally possible to use either a weak alkali (sodium carbonate) for a long batching time or a strong alkali (sodium hydroxide) for rapid fixation. It is claimed that the versatility of monofunctional dyes of this established type makes the more expensive bifunctional types unnecessary [160]. Detailed studies of each dye in the range led to the generation of a series of three-dimensional graphs from which a computer-based optimised system has been developed and made available to dyers.

The Levafix E/EA/EN (DyStar) system based on computer-centred optimisation is also available [161]. Two main alkali formulations are involved:

(1) Sodium carbonate with or without sodium hydroxide
(2) Sodium silicate with or without sodium hydroxide.

In general the prospect of working without silicate is regarded as a major advantage because the padding and washing-off of sodium silicate places considerable stresses on the machinery and on effluent treatment. However, the use of silicate in no way impairs the performance of Levafix dyes. Six optimised alkali recipes for this system are shown in Table 12.17, whilst Table 12.18 shows the relation between pad liquor pH, batching time and pad liquor stability.

Continuous dyeing with Sumifix Supra (NSK) heterobifunctional dyes is claimed [162] to give reproducible dyeings exhibiting a high degree of fixation and good wet fastness. The dyed fabric has an attractive handle and good appearance. The high fixation contributes advantageously to low effluent loading. Typical pad liquor formulations and fixation conditions, in comparison with those for aminochlorotriazine and vinylsulphone dyes, are given in Table 12.19.

There is a general tendency to abandon the 'classical' continuous reactive dyeing processes in favour of shorter pad–dry processes that is mainly driven by environmental and economic factors [163,164]. Particularly pertinent to this trend is the marked decrease in average length of run to a given shade. The latest developments in dyeing machinery allow greater control of the dyeing parameters and eliminate the former need for lengthy and

Table 12.17 Optimised alkali recipes for Levafix (DyStar) dyes at various applied depths [161]

Recipe	Dye conc (g/l)	5	10	20	40	60	80	120
A	Sodium carbonate (g/l)	5	10	20	40			
	pH 11.3							
B	Sodium carbonate (g/l)	10	20	20	20	20		
	Caustic soda 45% (ml/l)	0.2	0.35	0.65	1.3	2.15		
	pH 11.5–12.1							
C	Sodium carbonate (g/l)	10	20	20	20	20	20	20
	Caustic soda 45% (ml/l)	0.35	0.65	1.3	2.6	4.0	5.3	7.9
	pH 11.8–13.2							
D	Sodium carbonate (g/l)			17	13.5	10.5	7	4
	Caustic soda 45% (ml/l)			2.0	4.3	6.3	8.6	10.6
	pH 12.6–13.5							
E	Sodium silicate 37°Be (g/l)	40	40	40	80	100	100	100
	Caustic soda 45% (ml/l)	2.0	3.3	5.6	8.9	11.7	13.2	14.9
	pH 11.5–13.0							
F	Sodium silicate 37°Be (g/l)	25	25	25	40			
	pH 11.0							

Table 12.18 Relation between pad liquor pH, batching time and pad liquor stability for five optimised alkali recipes and Levafix (DyStar) dyes [161]

				Batching time (hours)	
	Recipe	pH	Pad liquor stability (min)	Bleached cotton	Mercerised cotton
Sodium carbonate without caustic soda	A	11.3	142	21	14
Sodium carbonate with a little caustic soda	B	11.9	41	14	8
Sodium carbonate with increasing caustic soda	C	12.2	18	10	6
Increasing caustic soda, decreasing sodium carbonate	D	12.7	8	5	3
Sodium silicate with increasing caustic soda	E	12.0	37	5	3

Table 12.19 Pad liquor formulations and fixation conditions for application of monofunctional and heterobifunctional reactive dyes by three continuous dyeing methods [162]

	One-bath pad–thermofix		One-bath pad–steam		Two-bath pad–steam	
Reactive system	Temp. / time	Alkali	Temp. / time	Alkali	Temp. / time	Alkali
ACT	200 °C 30 s	Na_2CO_3 10–20 g/l Urea 100–200 g/l	103 °C 5–10 min	Na_2CO_3 10 g/l	103°C 60 s	NaOH 40°Be 20 ml/l NaCl 300 g/l
VS	150 °C 60 s	Na_2CO_3 10–30 g/l Urea 50–100 g/l	103 °C 3–8 min	Na_2CO_3 6–12 g/l	103°C 30 s	NaOH 40°Be 20 ml/l NaCl 250 g/l
ACT-VS	180 °C 30–60 s	Na_2CO_3 10–20 g/l Urea 50–100 g/l	103 °C 1–5 min	$NaHCO_3$ 10–20 g/l	103°C 30–60 s	NaOH 40°Be 10 ml/l Na_2CO_3 20 g/l NaCl 100–150 g/l

ACT	Aminochlorotriazine
VS	Vinylsulphone

expensive conditioning of machinery at the beginning of each run. Liquor wastage is a major factor both economically and environmentally in continuous dyeing. Downtimes up to 60 minutes and waste liquor volumes up to 120 litres have been typical for traditional long runs to a shade [164]. Developments have reduced downtimes to as brief as 5 minutes and computerised systems inform management of the quantity and composition of pad liquors so that wastage is minimised to about 20 litres. By adopting pad–dry–bake or simple pad–dry methods chemical padding and steaming stages are eliminated, thus benefitting the environment by avoiding the demand for large amounts of salt.

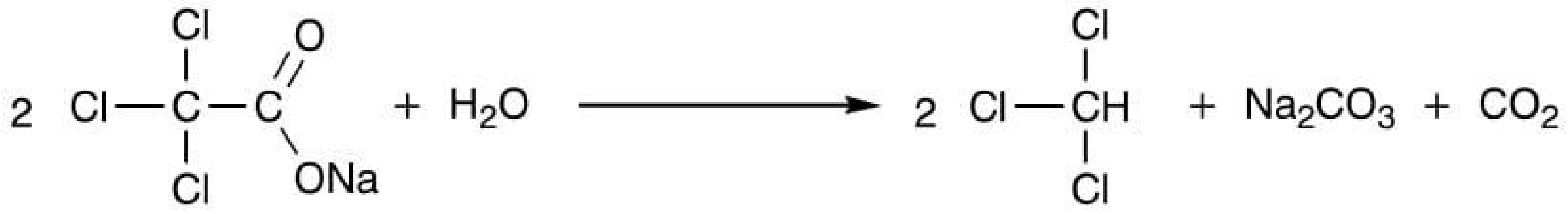
A typical development in this area is the Econtrol (Monforts and Zeneca) system [163,164], which consists of padding with dye, 1–2 g/l wetting agent and the alkali. With high–reactivity dichlorotriazine dyes this can be sodium bicarbonate (10 g/l). No urea, sodium silicate, electrolyte or other chemicals are required. After a short air passage the uniformly squeezed fabric is passed through a hot flue in which the carefully controlled relative humidity (25% moisture by volume) brings about fixation in two minutes. The humidity fulfils the function that otherwise would be provided by an environmentally problematical hydrotrope such as urea. This reduction of chemical consumption is indeed a major economic and environmental benefit.

Acrylamide-based migration inhibitors are claimed to give more efficient fixation [165]. A comparison of the differences between cotton and viscose has revealed [157] that viscose requires significantly longer immersion times. For example, immersion time for thoroughly prepared cotton can be less than one second on today's high-speed ranges, whereas 1–1.5 seconds is preferable for viscose. Contrary to some views, the addition of urea does not shorten immersion times and can in fact lengthen them [157].

Printing

Similar general considerations apply to direct printing processes as to continuous dyeing. A single all-in or a two-stage, pad–steam process may be used. Alginates are the preferred thickeners because other carbohydrates react with the dyes. The non-reactivity of alginates, in spite of their hydroxy groups, is thought to be due to the presence on each mannuronic unit of a carboxyl group that tends to repel the dye anions. As discussed in section 10.8.1, difficulties in obtaining alginates have led to the evaluation of alternatives, in particular the synthetic anionic poly(acrylic acid) types that give higher colour yields but can be more difficult to wash off. These products have been slow to replace the alginates apparently because the synthetic acrylic thickeners show varying sensitivity to electrolytes. However, detailed comparative rheological studies [166] have indicated that even if electrolyte sensitivity were controlled the acrylic polymers might still prove unsuitable despite the greater fixation that they give. At the slow printing speeds necessary in these laboratory studies the amount of paste absorbed by the fabric was always greater with the synthetic thickener, but this effect did not give higher colour yields because penetration was greater. It was concluded, therefore, that synthetic thickeners should not be adopted because of the higher dye consumption that outweighs any price advantage offered by the synthetic thickener. This is expected to be even more relevant at the high printing speeds necessary in commercial production, because of the greater shear-thinning of the synthetic thickener under these conditions of application [166].

Emulsion thickenings, either oil-in-water or water-in-oil and including half-emulsions, have been important in the past but are now much less popular on environmental grounds. Hydrotropes and a mild oxidising agent such as sodium *m*-nitrobenzenesulphonate are commonly added, the latter to protect azo dyes from reductive decomposition. Choice of alkali depends on the reactivity of the dye. Sodium bicarbonate is usually preferred, being cheap and offering high print paste stability with all but the most reactive dyes, but for dyes of sufficiently high stability the stronger alkalis (sodium carbonate or sodium hydroxide) may be chosen to provide higher colour yields under more alkaline conditions. The amount of bicarbonate may be reduced with highly reactive dyes. A pH-shift agent such as sodium trichloroacetate can be selected; this hydrolyses during steaming to release sodium carbonate (Scheme 12.5). However, another product of this hydrolysis reaction is chloroform. As well as being a volatile AOX-generating compound, chloroform is hepatotoxic and its use may be severely restricted.



Scheme 12.5

In the two-stage process the dyes are first applied without alkali, using a thickening agent such as sodium alginate that gels on subsequent application of alkali, usually together with electrolyte. High concentrations of sodium silicate (Na_2O/SiO_2 = 1:2.1, 47°Bé) or mixed alkali solutions (for example, 185 g/kg sodium carbonate + 185 g/kg potassium carbonate + 30 g/kg sodium hydroxide 32.5% or 38°Bé) are often used.

Undoubtedly of greatest concern in the printing of cellulosic fibres with reactive dyes is the essential demand for large quantities of the hydrotrope urea (typically 80–200 g per 1000 g of print paste). This auxiliary forms hydrogen bonds with water molecules, assisting in swelling of the fibre and the thickener, dissolution of the dyes and promotion of interaction between dye and fibre [167]. The most obvious benefits provided by urea are improved levelness, diffusion and colour yield but this compound is now environmentally suspect. Various attempts to replace urea over the last decade have led to contradictions, ranging from claims of complete success to the viewpoint that it has not yet been possible to find a satisfactory alternative and the prognosis for doing so is not particularly good.

Claims have been made [168] that the two-phase flash age process is the only way to avoid urea problems. In this process, no urea or alkali is present when printing is carried out initially, followed by padding with alkali and perhaps electrolyte (to limit migration) prior to steaming. However, even this approach has its ecological drawbacks due to the alkali (which may include silicate) and electrolyte. Furthermore, not all dyes give a satisfactory response, in particular phthalocyanine turquoise blues [167]. It is possible to improve the versatility of the process by including small amounts (up to 50 g/l) of urea; whilst this does not attain the environmental objective of totally avoiding urea, it does give an improvement over more conventional procedures. Suitable recipes are given in Table 12.20.

In conventional processes, the moisture content of the fabric at the fixation stage is about 20% or even less. However, in the flash age process it is significantly greater than this and the extent to which urea usage can be minimised is closely related to the amount of moisture present. Whilst traditional flash agers operated at around 50% humidity, more

Table 12.20 Print paste and fixation pad liquor formulations for two-phase flash age printing with reactive dyes [29]

Print paste recipe	
Urea	0–50 g
Sodium m-nitrobenzenesulphonate	10 g
Sodium alginate thickener	400–500 g
Water	440–590 g
	1000 g
Fixation pad recipe	
Potassium hydroxide	185 g
Sodium carbonate	185 g
Sodium hydroxide 38°Be	30 g
Water	600 g
	1000 g

recent attempts to eliminate urea have seen increases in this level. For example, the inclusion of humidifying or moisturising equipment in front of an ager to increase moisture content by 30%, aided by adjustment of the viscosity of the thickener, gave satisfactory yields in the absence of urea, even with phthalocyanine turquoise blues [167]. One means of increasing moisture content in the single-phase system of printing is to pre-wet by means of foam [169]. This enables the complete elimination of urea, giving additional advantages of better flow properties of the print paste, shorter fixation times, reduced water consumption and savings of thickener. In another approach, the concentration of urea could be considerably reduced by minor additions to the print paste of cyclodextrin, chitosan derivatives or so-called 'superabsorbers' based on acrylates [170].

However, after careful consideration of the various roles played by urea, it was concluded that the prospects of finding an adequate substitute are not promising [171]. This echoes earlier views [172] resulting from a study of the fixation of reactive prints with various concentrations of urea by saturated (102 °C) or high-temperature (120 °C) steaming. It is important to remember that urea functions not just by attracting moisture but also by entering into various interactions with dyes, thickener and substrate. As regards environmental aspects, the use of print paste preservatives, as discussed in section 10.8.6, should be borne in mind.

Conventional reductive discharge prints are applicable on grounds dyed with reactive dyes, especially if vinylsulphone dyes have been used, but there are difficulties with those non-azo blue and turquoise dyes that cede preference to resist processes [29]. Resists can be achieved by printing with a thickened paste containing a non-volatile acid (tartaric or citric acid, for example) or with an acidic salt such as sodium dihydrogen orthophosphate. The thickening agent used must be stable to acid; hydroxyethyl or methoxyethyl cellulose ethers, locust bean gum or tragacanth are suitable. The pre-printed and dried resist areas are then overprinted or padded with a solution of a highly reactive dye together with the minimum amount of sodium bicarbonate.

The washing-off process

An especially important and critical aspect of the application of reactive dyes, whether by dyeing or printing, is the washing-off process necessary to remove unfixed or hydrolysed dyes, as well as other products such as alkali, electrolyte and thickening agents. After rinsing to remove the more readily soluble products such as alkali and electrolyte, the goods are soaped at a temperature close to the boil to remove the unfixed active or hydrolysed dyes; a high temperature is necessary to remove hydrolysed dye from the interior of the fibres. Surfactants, especially nonionic types, are often added to the soaping liquor and a sequestering agent is added if the water is hard. Where thickening agents have been used, sufficient time must be allowed during the initial rinsing for the thickener to become hydrated and easier to remove.

This seemingly straightforward washing-off process has enormous environmental impact and has generated much research over the last few years. Washing-off accounts for as much as 50% of the processing cost of a reactive dyeing in terms of the washing-off process itself and subsequent treatment of the effluent. In addition to these environmental and economic consequences, the efficiency of washing-off has a critical influence on the fastness levels attained. Herein lies the primary rule: the extent of the washing-off sequence should be just sufficient to achieve the target fastness properties, since any further washing treatment only leads to unnecessary expenditure and greater effluent volumes. Seven parameters have been listed [173] as pertinent to the effects and efficiency of washing-off:

(1) number of washing baths
(2) duration of washing, varying in practice from a few seconds (continuous) to many minutes (batchwise)
(3) temperature, varying from rinsing at about 20 °C up to soaping at the boil, or higher in special circumstances
(4) liquor ratio, varying from 5:1 (continuous) to 100:1 (batchwise)
(5) mechanical movement of liquor and/or goods is of major importance in influencing liquor interchange
(6) composition of wash liquor: the electrolyte and chemical content of dyeings varies widely and these contaminants, together with any auxiliaries added to the washing baths, will considerably influence the result
(7) the substantivity of the reactive dyes present markedly influences their washing-off behaviour.

As a general illustration of the main effects, Table 12.21 shows the effect of a single washing treatment of varying time and temperature on an exhaust dyeing of the monoazo J acid scarlet CI Reactive Red 123 and a continuous dyeing of the copper formazan CI Reactive Blue 104. Both dyes contain a chlorodifluoropyrimidine reactive group, but consistently more dye was removed from the continuous dyeing, especially for shorter times at the lower temperatures. Even after six successive washes at 25 °C, the removal of unfixed dye from the exhaust dyeing only increased to 56, 62 and 74% respectively from the 24, 36 and 52% shown for one wash [173]. In general, these results emphasise the importance of longer times and higher temperatures. Further results demonstrated that electrolyte additions up to 10 g/l did not markedly influence the removal of dye but showed significantly increased effects at 20 g/l and especially 50 g/l. Mild alkaline washing was just as effective as mild acidic washing and the addition of a nonionic agent had a favourable influence on dye removal. These results are specific to the two dyes evaluated. However, it is abundantly clear from these trends and comments, bearing in mind the wide variety of reactive dyes, substrates and machinery, that optimising the washing-off procedure in each case for maximum economy and minimum environmental impact is no easy matter.

Table 12.21 Effect of a single washing treatment for various times at various temperatures on the removal of unfixed dye from exhaust or continuous dyeings with chlorodifluoropyrimidine reactive dyes [173]

	Removal (%) of unfixed dye from exhaust or continuous dyeing					
Washing	Exhaust dyeing of CI Reactive Red 123 on bleached cotton			Continuous dyeing of CI Reactive Blue 104 on mercerised cotton		
Temperature	25 °C	70 °C	98 °C	25 °C	70 °C	98 °C
Time 15 s	24	64	84	38	80	86
1 min	36	74	88	52	90	90
5 min	52	90	92	74	92	94

These difficulties have been thoroughly discussed in an exhaustive study [174]. Theoretical considerations were thoroughly explored and the economic and technical merits of four different washing systems were analysed:

(1) individual washing baths
(2) dyeing machines operating with continuous liquor exchange
(3) continuous rope-washing machines
(4) open-width washing machines.

Three key stages applicable to most washing processes were identified:

(1) In the first stage, unfixed dyes, salt and alkali present in the liquor phase must be removed and this is best done by replacing this liquor with fresh water. Sorption, desorption and diffusion processes play only subordinate roles in this stage, the key factors being liquor flow, mechanical action and liquor exchange. The dilution laws are generally applicable.
(2) In the second stage, substantial amounts of alkali and unfixed dyes are desorbed and diffuse from the fibre pores into the liquor phase. This is the diffusion stage and the rate-determining step is diffusion of the labile dye molecules out of the fibre phase. This takes time and is accelerated by higher temperatures and perhaps by mechanical agitation of the substrate.
(3) In the final stage, the electrolyte and unfixed dye concentrations are low but further changes of liquor must take place until almost all the unfixed dye molecules are desorbed.

These three processes are not necessarily distinct consecutive stages but are major identifiable events that may be more or less separated or interlinked by transitional steps. It is argued that the washing-off requirements are different in each stage. In the first stage of liquor exchange, cold rinsing is preferred because higher temperatures offer only a slight advantage and alkalinity may hydrolyse dye–fibre bonds. Empirically, this stage may be regarded as completed when the electrolyte content reaches about 1 g/l; the number of liquor changes required is related to liquor ratio. A shorter liquor ratio demands more changes and involves only slightly lower water consumption, so is without advantage at this stage. Continuous methods are more effective, since these give direct displacement of contaminated liquor by fresh water, rather than mixing of them. In the second stage of diffusion from the fibre, hot washing is necessary to ensure the major advantage of more rapid diffusion. Individual dye properties, such as substantivity and diffusion coefficient, are particularly pertinent here. In contrast to earlier conclusions [173], these studies involving several surfactants showed no particular advantage from the use of detergents [174]. The addition of a detergent is best avoided if possible, since it further contaminates the effluent. It is useful to compare the economics and fastness performance, particularly in heavy depths, of a thorough washing-off against a less than complete extraction of unfixed dyes followed by a cationic aftertreatment.

To minimise effluent problems by treatment of liquors before discharge to effluent, it is preferable to concentrate the residual dyes in as small a volume as possible. This implies that removal of unfixed dyes should be restricted to as few baths as possible. In this context dye substantivity is an important consideration [175]. Cold initial rinsing removes much of the low-substantivity dye present but dyes of high intrinsic substantivity are difficult to remove in this way. If the initial rinse is hot, however, even these high-substantivity products are effectively removed, thus achieving concentration of these dyes in the initial stage and ensuring easier subsequent removal. Thus it was proposed that washing-off could be improved by using a hot rather than a cold initial wash [175]. This was substantiated in further optimisation studies which enabled the residual dyes to be confined to two or three baths, surfactant additions not being necessary for these water-soluble contaminants. These results were confirmed in bulk processing. It was found that lower liquor ratios were beneficial in washing-off [176] and similar control parameters were identified in continuous washing-off [177]. The benefits of hot initial washing (60–70 °C) have been demonstrated in yarn package dyeing, emptying of the vessel after dyeing being unnecessary [178].

From the viewpoint of energy conservation, the washing temperature should be chosen according to the dyes present [179]. Since dyes of low substantivity are desorbed more readily under mild conditions, a lower temperature should be selected for these dyes and higher temperatures for dyes of higher substantivity. In an evaluation of the washing-off behaviour of dichlorotriazine dyes from cotton at temperatures ranging from 20 to 98 °C with water alone, and at 98 °C with a surfactant, the surfactant-aided method was found to be the most effective [180] and the benefits of aftertreating with cationic agents were confirmed.

A detailed comparison [181] of three vinylsulphone dyes included a low-substantivity monoazo *N*-acetyl H acid derivative (CI Reactive Red 35), a monoazo *N*-acetyl J acid type of higher substantivity (CI Reactive Orange 82) and a phthalocyanine turquoise somewhat prone to aggregation (CI Reactive Blue 21). Dyeings of these individual products were subjected to three wash-off procedures:

(1) conventional sequence: cold, cold, warm, hot, cold
(2) cold/hot sequence: 30 °C, followed by several baths at 95 °C
(3) hot sequence: repeated treatments at 95 °C.

Typical results are given in Table 12.22. The objective was to examine the relationship between the substantivity of the unfixed dyes and their response to changes in the conditions of the washing sequence.

Table 12.22 Effects of various washing–off sequences on the rate of desorption of dye in successive washing baths and the degree of staining of adjacent material in washing tests [181]

		*Colour value of wash liquor			Fastness to washing		
Washing sequence		(1)	(2)	(3)	(1)	(2)	(3)
CI Reactive Red 35 (low substantivity) W = 510 nm							
Washing bath	1	16	15	18	2	2	3
	2	2	2	1	3	4	4
	3	2	1	0	4	4–5	4–5
	4	1	1	0	4–5	4–5	4–5
CI Reactive Orange 82 (moderate substantivity) W = 490 nm							
Washing bath	1	17	23	56	1	1	2
	2	10	31	4	1–2	3	3–4
	3	11	2	0	2	4	4–5
	4	13	0	0	3–4	4–5	4–5
	5	2	0	0	4–5	4–5	4–5
CI Reactive Blue 21 (phthalocyanine type) W = 664 nm							
Washing bath	1	14	15	33	2	2	2–3
	2	3	15	6	2–3	3	4
	3	2	2	1	2–3	4	4–5
	4	6	0	0	3	4–5	4–5
	5	3	0	0	4	4–5	4–5

* Colour value given by 1000 E/d, where E is extinction at the peak wavelength (W nm) and d mm is the cell thickness

The low-substantivity red dye was desorbed relatively quickly, mainly in the initial cold rinse, and the acceptable fastness rating of 4–5 was reached after three or four washing baths. The greater difficulty of desorbing the more substantive orange dye was clearly evident. Only after the first hot bath of the sequence was most of the unfixed dye desorbed. A fastness rating of 4–5 was reached after the 5th, 4th and 3rd baths respectively of the washing sequences (1), (2) and (3). With CI Reactive Blue 21 seven baths were needed in the conventional sequence (1) to give a fastness rating of 4–5. Sequences (2) and (3) were more effective, giving acceptable fastness after four and three baths respectively. In all cases it is the hot washing sequence (without surfactant) that enables this target to be reached quickly and with the lowest water consumption. It was confirmed that the final bath need not be absolutely colourless after washing, nor is complete removal of unfixed dye necessary to attain the target fastness level.

Similar results have been observed in the washing-off of reactive prints, in which it is necessary to monitor the removal of the alginate thickener as well as desorption of the unfixed dyes [182]. Batchwise washing showed that the thickener was rapidly washed out and that elevated temperatures increased the rate of removal. No significant dwell time for thickener swelling seemed to be necessary. Significantly more effective removal of thickener with increasing temperature was observed in continuous washing and most of the thickener was eliminated in the first wash.

Confirmation of earlier work [180] on the temperatures of washing-off of dichlorotriazine reactive dyeings on cotton revealed that surfactant and sodium carbonate together were more effective than water alone, although there was little difference in performance between the six surfactants examined [183]. However, the addition of surfactant did not appear to be essential in order to achieve adequate dye desorption and fastness to washing, 2–5 g/l sodium carbonate being sufficient. These results were later substantiated with dichlorotriazine dyeings on lyocell [184] and for aminochlorotriazine dyeings on cotton [185].

Further studies involved different alkalis (ammonia, sodium bicarbonate, potassium hydroxide and sodium hydroxide) and unspecified buffers covering the range pH 7–13 with aminochlorotriazine dyeings on cotton. Although all these alkalis and buffer solutions were capable of removing unfixed dyes, the effectiveness of washing-off of the systems varied; potassium hydroxide and sodium bicarbonate were the most effective and the pH 8 buffer solution was the least. In general, effectiveness increased with increasing pH but the outstanding behaviour of potassium hydroxide and sodium bicarbonate could not be explained in terms of pH alone. Despite varying effectiveness in terms of washing-off, all of the washed dyeings were virtually identical in fastness to washing. When multiple alkaline washes were evaluated on aminochlorotriazine dyeings, potassium hydroxide and sodium carbonate were the most effective, although sodium bicarbonate was more attractive in terms of low cost, environmental impact and fastness to washing. However, some of these multiple alkaline treatments showed evidence that dye–fibre bond cleavage may have taken place in addition to removal of hydrolysed dye [185].

When washing-off in a jet machine, a combination of liquor exchange and continuous overflow rinsing is advantageous [186]. Optimal rinsing procedures depend on machine parameters and the cost structure of the plant, but in general the most economical system appears to be:

(1) liquor exchange rinsing initially (salt removal)
(2) continuous rinsing at a higher temperature (diffusion of unfixed dye)
(3) liquor exchange rinsing finally (removal of dye liquor).

The objective of stage (1) is to lower the salt concentration to 1–2 g/l and this requirement determines the number of initial baths given before subjecting the dyeing to a higher temperature. Salt removal is accelerated by liquor changes and dilution before commencing continuous rinsing. The duration of continuous rinsing is adjusted according to the depth of shade and the known diffusion properties of the dyes present. Calcium and magnesium ions present when washing in hard water make the unfixed dye anions more difficult to remove; poly(acrylic acid) derivatives are effective sequestering agents in mildly alkaline liquors [187].

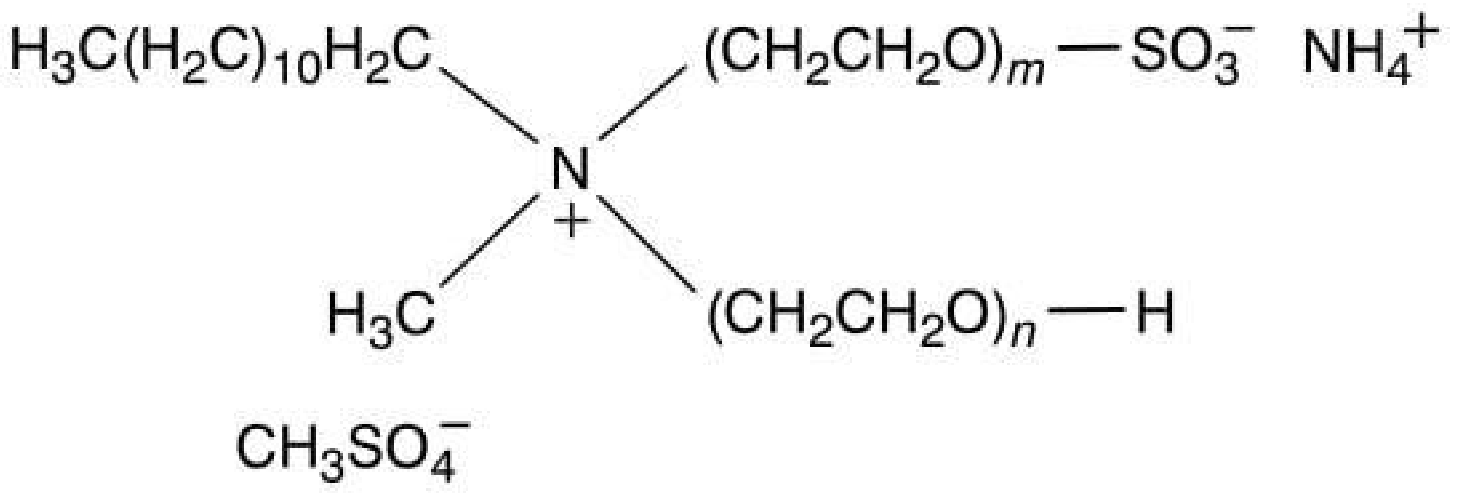
Stripping

The stripping of cellulosic materials dyed with reactive dyes is carried out by alkaline reduction followed by hypochlorite oxidation, preceded by a boiling treatment with EDTA if metal-containing dyes have been used. For example, a treatment with 5 g/l sodium carbonate or sodium hydroxide and 5g/l sodium dithionite at the boil is followed by a treatment in 0.5–1 °Tw hypochlorite, an antichlor and thorough rinsing.

12.7.2 Wool

Although wool can be dyed with typical reactive dyes produced essentially for cellulosic substrates, the adoption of reactive dyes on wool has depended on the development of special ranges of dyes capable of covalent bonding under slightly acidic conditions. The use of surfactant auxiliaries is essential. The types of dyes used and the mechanisms of reaction have been discussed in section 7.7 and elsewhere [2]. These dyes are generally similar in response to dyebath pH to milling acid dyes, medium or full depths being applied at pH 5.0–5.5 and pale depths at pH 5.5–6.0. At lower pH values adsorption and fixation may be irregular, whilst at higher values exhaustion is poor. Even at optimal pH fixation may still be incomplete within normal dyeing times, particularly when dyeing navy or black shades. Hence the bath is adjusted to a weakly alkaline state, which ensures complete fixation as well as helping to remove hydrolysed dye. A typical procedure is to dye at the boil and pH 5, followed by cooling to 80 °C and adjustment of the pH to 8.0–8.5 with ammonia, after which treatment is continued for some 20–30 minutes at 80 °C.

A surfactant auxiliary is necessary to prevent tippy or skittery dyeing. Cationic or nonionic products have been used but the most useful have been the amphoteric *N*-alkylbetaines and alkylamidobetaines (described in section 9.7) and ethoxylated amphoteric types represented by structure 12.41 [188]. Compounds of this type can interact under slightly acidic conditions with both fibre and dye. The mechanisms have been investigated in detail [188–192]. The initial step appears to be the formation of an auxiliary–dye complex by interaction between the quaternary group in the surfactant and the dye anion, such a complex being less soluble than the dye alone. As the concentration of the auxiliary is increased to an excess over that required for complexing with the dye anions present, surfactant micelles are formed that tend to solubilise the auxiliary–dye complex. Unlike most levelling agents these amphoteric products often increase the rate of wool dyeing, to an extent dependent on the chemistry and concentration of the auxiliary and of the dye. Conversely, they may have a retarding effect if the concentration of auxiliary is so high as to solubilise the auxiliary–dye complex completely. These auxiliaries also tend to improve dye exhaustion at equilibrium.



12.41

($m+n$ = 10–80)

The accepted explanation for this behaviour is that the zwitterionic auxiliary–dye complex is less electronegative than the dye anion; hence it exhibits more hydrophobic characteristics with increased molecular size and lower aqueous solubility. Consequently, the affinity of the dye for the undamaged roots of the wool fibres is enhanced relative to that for the more hydrophilic damaged tips. The auxiliary–dye complex is less sensitive to root-tip differences and thus gives more level dyeing. Furthermore, adsorption of the auxiliary by the fibre increases the electropositive charge on the fibre, thus increasing the attraction for anionic dyes. This will tend to further increase the rate of dyeing and is also the mechanism whereby the total amount of dye absorbed is increased. On the whole, there is little evidence that these agents increase migration and indeed no migration can take place once the dye has reacted covalently with the fibre.

The levelling action of betaines increases with concentration and with increasing length of the alkyl chain [188]; the effects on rate and total absorption disappear with products containing a very long alkyl chain (about C_{16}) at a high concentration, although the levelling properties are maintained irrespective of the rate effects. In general, the betaines bring about a greater change in sorption characteristics than do the ethoxylated amphoteric compounds of similar alkyl chain length [188]. Thus higher concentrations of the latter are necessary to produce a similar effect; this can be an advantage, since the effects are not then so critically sensitive to the concentration of auxiliary. Furthermore, the manufacturer can vary the balance of properties of the auxiliary by varying the length of the oxyethylene chains as well as of the alkyl group.

Using laser Raman spectroscopic techniques, it was confirmed that the primary mechanism involves ionic interaction between the anionic sulphonate groups of the dye and the cationic quaternary group of the auxiliary, although hydrophobic interactions were also significant [190]. However, investigations of the coverage of damaged wool indicated that interaction of the auxiliary with the fibre is mainly responsible for the improvement in levelness, both the surface and the interior of the fibre being involved [191]. Dye–auxiliary interaction does not seem to play a major role in levelling out root-to-tip variations. Studies with variously modified wools, including wool pretreated with an amphoteric agent, demonstrated that these auxiliaries mainly accelerate the rate of exhaustion on normal wool, whereas the effects on modified wools are minimal [192]. Although these agents promote dye uptake and fixation on normal wool, they do not enhance dye uptake to the same extent on Hercosett-treated wool [2].

Traditionally, the alkaline treatment given after reactive dyeing has been with ammonia at pH 8.0–8.5 and this is still the favoured method of removing unfixed dyes, although sodium bicarbonate is occasionally used. Indeed, it is claimed that the lower basicity of bicarbonate results in less fibre damage and no detrimental effect on fastness properties [193]. A specific disadvantage of ammonia is that it can cause uneven treatment in different parts of a yarn package because of irregular swelling of the fibre [2].

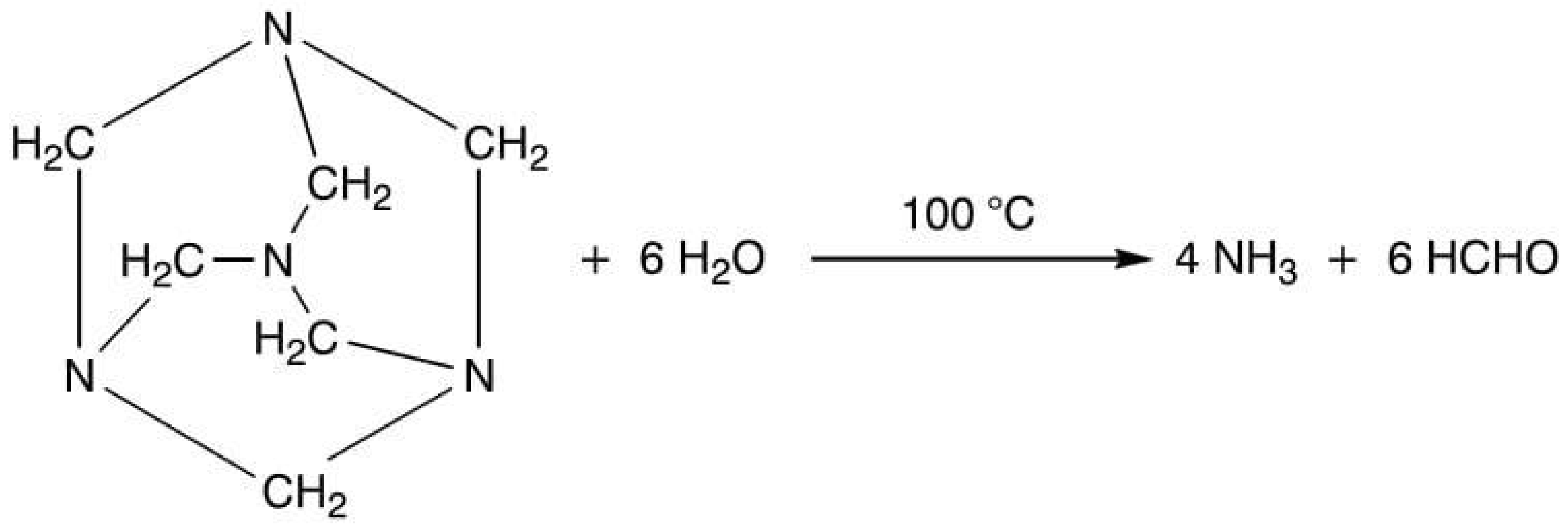
Several other agents have been suggested as potential aftertreating agents for reactive-dyed wool:

(1) Hexamethylenetetramine: this ammonia precursor does not cause fibre swelling and the unfixed dyes are removed efficiently at pH 6.5, compared with pH 8.5 with ammonia, thus causing less damage to the wool. However, the hydrolysis of this compound (Scheme 12.6) results in the formation of formaldehyde and this can modify the hue of certain dyes [2].

(2) Sodium bisulphite: this additive reacts by nucleophilic addition to the vinylsulphone group of dyes of this type, decreasing the substantivity and increasing the aqueous solubility of the unfixed dyes (Scheme 12.7).

(3) A commercially branded product believed to be sodium trichloroacetate: this is added at a concentration of 5% to the dyebath 20 minutes before the end of dyeing. Sodium carbonate is formed by hydrolysis of the trichloroacetate (Scheme 12.5), accompanied by a change of pH from 5.0–6.0 to 6.7–6.9 [2]. This reaction also releases the volatile AOX-generating chloroform, however.

(4) Various amine salts, such as hydrochlorides of 1,6-diaminohexane, 1,12-diaminododecane, 1-aminododecane and a bisulphate adduct of 1,6-di-isocyanatohexane. This was an attempt to introduce a final reactive step to form crosslinks between unfixed dye molecules on the fibre [193].



Scheme 12.6

$$[\text{dye}]{-}\text{SO}_2\text{CH}{=}\text{CH}_2 + \text{NaHSO}_3 \longrightarrow [\text{dye}]{-}\text{SO}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{Na}$$

Scheme 12.7

Although all of these compounds were applicable in principle, treatment with sodium bicarbonate offers a much more economical and reliable option.

The mechanism of reaction of α-bromoacrylamide dyes with wool has been investigated [194]. The application to wool of a range of heterobifunctional dyes normally used on cellulosic fibres has been promoted recently [195]. These dyes offer high exhaustion and fixation, as well as exceptional fastness. They are relatively insensitive to dyeing variables and suitable for dyeing wool–cellulosic blends by a one-bath method, with savings in energy costs and less wool damage. The choice of auxiliaries is essentially the same as when applying these dyes to cotton, although the pH is varied according to whether wool or wool–cotton is to be dyed. An ammonia aftertreatment is recommended for wool dyeings. The reactive dyeing of wool at 110 °C and pH 4.5 (ammonium sulphate and acetic acid) in the presence of a betaine auxiliary has been described [196].

Reactive dyes can be applied to wool by printing [2,29]; suitable ranges include chlorodifluoropyrimidine, α-bromoacrylamide, sulphatoethylsulphone and aminochlorotriazine. A typical print paste recipe is shown in Table 12.23. Derivatives of locust bean or guar gum, either alone or in combination with water-soluble British gum, are the preferred thickeners. Humectants, particularly urea, are essential to aid solubilisation and penetration as well as swelling of the wool. A wetting agent (5–10 g/kg) may also be needed if chlorination of the goods has been less than optimum and where complete penetration of the print design is desirable. Antifoam addition is generally necessary in machine printing. A non-volatile acid such as citric acid or an acid donor such as ammonium tartrate or ammonium sulphate is normally required to give optimum pH conditions; however, vinylsulphone dyes are applied under neutral to slightly alkaline conditions using sodium acetate (40 g/kg). The oxidising agent sodium chlorate is often added to counteract the reducing effect of the wool, although if vinylsulphone dyes are printed under alkaline conditions sodium *m*-nitrobenzenesulphonate is effective in protecting any reduction-sensitive dyes.

Table 12.23 Typical print paste recipe for the printing of wool with reactive dyes [29]

Dye	*x* g
Urea	50 g
Thiodiethylene glycol	50 g
Thickener (10–12%)	500 g
Acid or acid donor	10–30 g
Antifoam	1–5 g
Water to	1000 g

The most important reducing agents used for discharge printing on wool are the formaldehyde-sulphoxylates [2]. These agents are restricted to the minimum effective concentration within the range 30–180 g/kg. The print is washed in several baths containing 2 g/l disodium hydrogen orthophosphate, ammonia (to give pH 9) and an anionic surfactant in successive baths at temperatures increasing from 40 to 80 °C. The printing of silk with reactive dyes, using sodium silicate as alkali and sodium alginate as thickener, has been described [197]. Problems arising from the contamination of effluents with reactive dyeing and printing auxiliaries represent an important issue that has been fully discussed elsewhere [198–201].

12.8 SULPHUR DYES

The application of sulphur dyes to cellulosic substrates involves conversion to the substantive leuco form by alkaline reduction, followed by oxidation on the fibre to the insoluble disulphide form (section 1.6.2). Consequently, reducing and oxidising agents are essential auxiliaries. Secondary auxiliaries include wetting agents, sequestering agents, antioxidants, electrolytes and hydrotropes. Useful reviews of developments in sulphur dyes and their application are available [30,202,203]. The concern here is with the essentials of the auxiliary agents used in their application. It is convenient to deal separately with the aspects of reduction and oxidation. The discussion is confined to application by dyeing since the use of sulphur dyes in printing nowadays is restricted mainly to sulphur blacks applied by techniques similar to those used in vat printing [29].

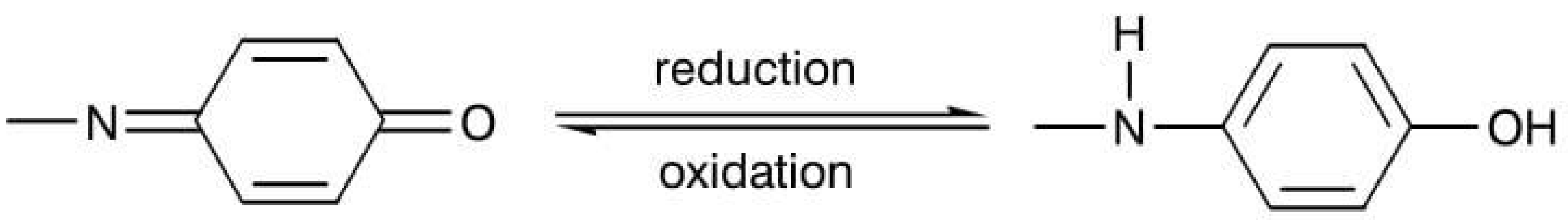
12.8.1 Reduction

Sulphur dyes in the insoluble disulphide form and the CI Solubilised Sulphur brands are reduced by the dyer as part of the application procedure. In the case of the CI Leuco Sulphur brands reduction has already been carried out by the manufacturer, so that they are substantially in a form suitable for immediate application (section 1.6.2) The chemistry of the reduction of sulphur dyes is complex, as is the chemistry of the dyes themselves; it has been well described elsewhere [204]. It is possible to describe the state of a reduced sulphur dye in alkaline sulphide or polysulphide solution by the general formula 12.42, but there are certain complications. In many cases the chromogen is not itself reduced, but in others, notably reddish browns, blues and navy blues based on indophenols, the chromogenic quinonimine grouping can be reduced (Scheme 12.8). Additionally, the value of n in structure 12.42 varies, even for a given dye. It is not surprising, therefore, that the amount of reducing agent (and alkali) required varies from dye to dye, depending on the chemistry of the dye as well as on the concentration in the formulation. Hence the manufacturer's literature must always be consulted for the amounts of auxiliaries to be used with particular dyes in the various batchwise, semi-continuous and continuous processes.

$$\mathrm{D}\left[\mathrm{S}_n-\mathrm{SX}\right]_m$$

12.42

D = chromogen
n = 0–5 $m \geq 1$
X = H or Na, depending on pH



Scheme 12.8

The reduction process is invariably carried out in an alkaline medium, partly because of the instability of most reducing agents at low pH and partly because the acidic thiol groups react with alkali to give the much more soluble anionic thiolate form [204]. Traditionally the most widely used reducing agents have been sodium sulphide (Na_2S) and sodium hydrogen sulphide (NaHS). Technically these are still the most widely preferred, not only for their efficacy but also because they are relatively inexpensive. Nowadays, however, they are increasingly subject to scrutiny on environmental grounds. At least 12 g/l sodium sulphide is required to dissolve the water-insoluble CI Sulphur dyes. The quantity added to the dyebath varies from dye to dye but is generally proportional to the amount of dye, with a minimum of 1.5–3.0 g/l [30]. When using sodium hydrogen sulphide the quantity is generally 0.6 times that of sodium sulphide, but it is also necessary to add alkali (10 g sodium hydroxide or 5 g sodium carbonate per 7 g sodium hydrogen sulphide). The pre-reduced CI Leuco Sulphur dyes usually contain a mixture of sodium sulphide and sodium hydrogen sulphide, together with hydrotropic and dispersing agents such as 2-ethoxyethanol, sodium 1,3-xylene-4-sulphonate, sodium *p*-toluenesulphonate and sodium tetralinsulphonate [202]. The quantities of sodium sulphide and sodium hydrogen sulphide referred to above relate to the full-strength concentrated products and must obviously be proportionately adjusted if weaker commercial brands are available.

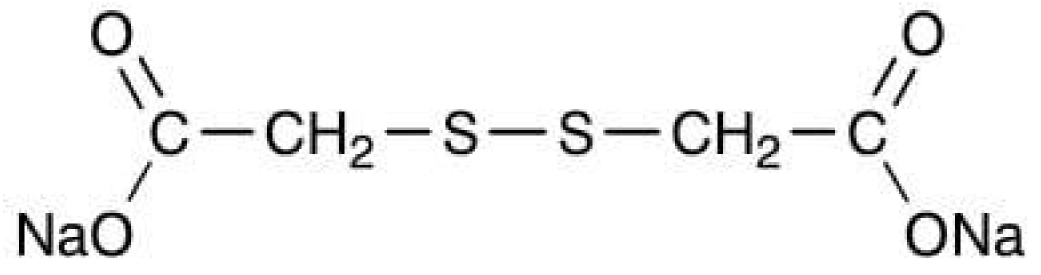
In some applications, particularly in jet and winch dyeing, there is a danger that the reducing agent may be prematurely oxidised by air. Antioxidants, added along with the dyes and the primary reducing agent at the beginning of dyeing, can be used as palliatives. Polysulphides of general formula 12.43, such as disodium tetrathionite, have been widely used for this purpose and provide improved dyebath stability. These additives can be used with other reducing agents described below but are not compatible with dithionite. Another approach is to add a relatively more stable alkaline reducing agent such as sodium dithiodiglycolate 12.44 [205].

Environmental concerns are gradually curtailing the use of sulphides as reducing agents [203,206], although it has been indicated [207] that as late as 1995 some 90% of all sulphur

$XO_3S-S_n-SO_3X$

12.43

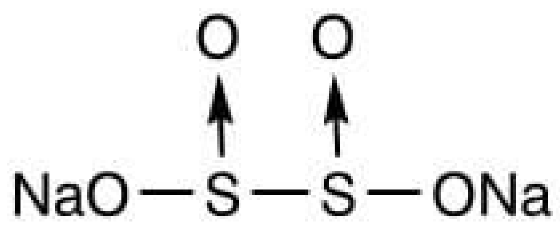
X = Na, K, H or NH_4
n = 1–4



12.44

dyes applied worldwide were still reduced by sulphides. The environmental problems arising from sulphides include the toxicity of hydrogen sulphide, corrosion of the effluent drainage system, damage to the treatment works and the often associated high pH and unpleasant odours [208]. Sulphides cause no odour nuisance above pH 9 but at neutral or acidic pH values gaseous hydrogen sulphide is liberated. Neutralisation or acidification can occur in the dyehouse or during waste stream mixing. The MAK value of hydrogen sulphide is 15 mg/m^3 (10 ppm), this being the maximum allowable concentration in the workplace at a continual contamination level to avoid impairment of health, the odour threshold being 0.035–0.14 mg/m^3 of air [207]. Polysulphides yield free sulphur on acidification and this can lead to odours of sulphur dioxide on the dyed substrate. Nevertheless, sulphides can be quantitatively removed before discharge to the effluent, albeit at a substantial cost [208,209].

Several reducing agents have been suggested as environmentally more acceptable alternatives to the alkali sulphides. All are more expensive and exhibit other disadvantages. For example, the reduction may be more difficult to control, or a particular agent may be effective only with a limited range of dyes. Even then the alternatives may be less effective than the alkali sulphides in terms of colour yield. Nor is the fact that such compounds do not generate hydrogen sulphide a guarantee of freedom from environmental problems; for example, some give quite high COD levels. The most obvious alternative is sodium dithionite (12.45) with alkali, the reducing agent most widely used with vat dyes (section 12.9). When used with sulphur dyes, however, the process is difficult to control and some dyes may be partly destroyed through over-reduction. Nevertheless, dithionite is effective with CI Solubilised Sulphur and sulphurised vat dyes.



$$NaO-\overset{\overset{O}{\uparrow}}{S}-\overset{\overset{O}{\uparrow}}{S}-ONa$$

12.45
CI Reducing Agent 1

Sodium hydroxide is the alkali usually used in conjunction with dithionite. Sodium carbonate is a possible alternative when CI Solubilised Sulphur dyes are used but is insufficiently alkaline for the CI Sulphur brands, requiring careful control if over-reduction and the associated lower yields are to be avoided [30]. Typical concentrations are given in Table 12.24. The system of sodium carbonate and sodium dithionite used to reduce blue and black CI Solubilised Sulphur dyes is particularly suitable for flame-retardant viscose fibres that are sensitive to strong alkalis, since it preserves a satisfactory level of flame retardancy [30]. It is also possible to use a mixture of dithionite with sodium sulphide in alkaline media.

Sodium formaldehyde-sulphoxylate (12.46; sodium hydroxymethanesulphinate) and alkali, although more stable than alkaline dithionite, tends to share the same disadvantages

Table 12.24 Typical applied concentrations of sodium dithionite and alkali for exhaust dyeing [30]

Liquor ratio 10:1	1% Dye	6% Dye
Caustic soda flakes	3.5 g/l	7.5 g/l
Sodium dithionite	2.5 g/l	7.0 g/l
These amounts are decreased by 30–40% at liquor ratio 20:1 or increased correspondingly at liquor ratio 5:1		
Sodium carbonate	0.5 –1.5 g per g of dye	
Sodium dithionite	0.25–0.75 g per g of dye	

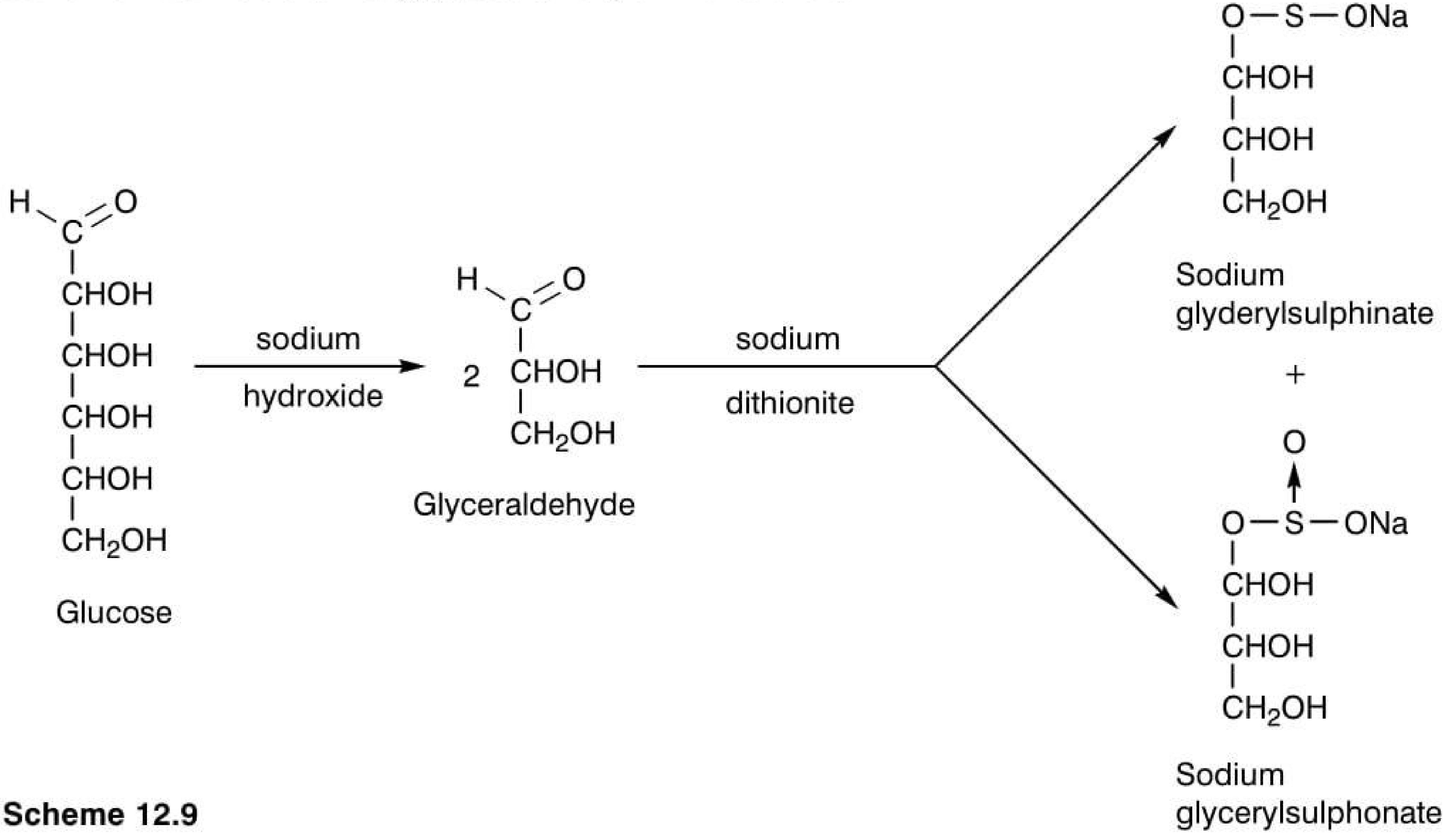
$$HOCH_2{-}O{-}S{-}ONa$$

12.46
CI Reducing Agent 2

and is rarely, if ever, used with sulphur dyes owing to associated handling difficulties, inadequate cost-effectiveness and poor efficiency [207]. Sodium dithiodiglycolate (12.44) was mentioned above as an antioxidant. Such compounds may be used as the primary reducing agent in conjunction with alkali. Although they do not give rise to environmentally undesirable inorganic sulphides in the effluent, their chemical stability results in a high chemical oxygen demand, often causing more problems than those arising with sodium sulphide [202]. This system is rarely used for much the same reasons as sodium formaldehyde-sulphoxylate [207].

The most promising alternative to sulphides, from an environmental point of view, is the use of the reducing sugar glucose with sodium hydroxide or sodium carbonate. This system does not satisfactorily reduce all dyes, however. It is reasonably effective with CI Solubilised Sulphur brands [210], with which it may be used either as the sole reducing agent or in conjunction with sodium polysulphide, usually resulting in increased dye yields. It can be used as an additional reducing agent with CI Leuco Sulphur dyes, thus giving a lower sulphide content in the dyebath, or together with sulphide or polysulphide in the reduction of the traditional water-insoluble CI Sulphur brands [30]. The system is pH- and temperature-sensitive; hence performance may be good on jet machines but poor on the more temperature-sensitive jigs. Typical quantities recommended for a batchwise dyeing method [30] at liquor ratios of 10:1 to 20:1 are 3–8 g/l glucose, 4–10 g/l sodium carbonate and 2–6 g/l sodium hydroxide, depending on applied depth, a pH of 11–12 and a minimum dyeing temperature of 90–95 °C being necessary [206].

The glucose reducing system has a characteristic odour of burning sugar that many people consider preferable to the odour of an alkaline sulphide bath, although others dislike it, finding it excessively sweet and nauseous [30]. Nevertheless, the versatility of glucose-based binary systems has been emphasised [207]. The major problem with an alkaline glucose system is that it is gradually transformed into various decomposition products, thus losing its reducing action. The intermediate by-products possess some reducing action but are not sufficiently stable. More stable decomposition products are formed if dithionite is added to the system, this being the subject of patents more than sixty years ago [207]. Scheme 12.9 has been suggested to explain this effect.



Scheme 12.9

The reduction potentials of various reducing agents listed in Table 12.25 show that at 50 °C the dithionite/glucose system has a potential that is only slightly lower than that of dithionite alone, even though glucose has the lowest potential in this series. The addition of glucose reduces the potential of sodium dithionite to the point where full colour yield is obtained without the risk of over-reduction. Dyeing tests have confirmed that although sodium dithionite alone is exceptionally concentration-sensitive, the addition of glucose gives a more stable system. Optimal colour yield and good reproducibility are obtained even if dyeing temperature, time and concentrations of chemicals fluctuate within certain narrow limits. Similar results have been obtained with other glucose binary systems, including hydroxyacetone or sodium formaldehyde-sulphoxylate as stabiliser.

Table 12.25 Reduction potentials of various reducing systems at 50 °C [207]

Reducing system	Reduction potential (mV) at 50 °C (platinum electrode)
Sodium formaldehyde-sulphoxylate	–900
Sodium dithionite	–850
Sodium dithionite/glucose	–700
Hydroxyacetone	–680
Sodium sulphide	–650
Sodium polysulphide	–500
Glucose	–200

5 g/l Reducing agent
10 ml/l Caustic soda 38°Be

The environmentally innocuous properties of reducing sugars have been claimed for the dyeing of jute with sulphur dyes [211]. This claim is based on the influence of citric acid addition on the hydrolysis of cane sugar, giving a higher proportion of reducing sugars (Table 12.26). The optimum addition is 0.04% citric acid and treatment of the coarse brown sugar from the sap of palm trees (so-called 'jaggery') is for 24 hours at ambient temperature, giving a product termed 'liquid jaggery'. This is added at 2.5 times the mass of sulphur dye in the dyeing of jute at 100 °C for 1 hour in a liquor containing 50 g/l sodium chloride. This product can also be utilised in printing, a typical print paste formulation being shown in Table 12.27.

Table 12.26 Effect of citric acid addition on the composition of cane sugar after hydrolysis [211]

		Composition of product	
Citric acid concentration (%)	pH	Reducing sugars (%)	Non-reducing sugars (%)
0	5.9	21	40
0.01	5.8	30	38
0.02	5.5	33	36
0.03	5.3	36	32
0.04	5.3	39	28
0.05	5.0	43	24

Table 12.27 Typical print paste formulation for the application of liquid jaggery as a reducing system for sulphur dyes [211]

Sulphur dye	3–5 g
Sodium carbonate	2–3 g
Liquid jaggery	7.5–12.5 g
Thickening agent	80 g
Water (if necessary) to	100 g

2-Mercaptoethanol (12.47) with alkali has been suggested as an alternative to sulphides [210], offering the advantages of no sulphides in the effluent and no odour from the dyebath, although the product itself can give off unpleasant and highly toxic fumes. This process is relatively expensive, with a tendency towards lower yields and a more restricted range of suitable dyes than when using traditional sulphides, so it has not achieved significant commercial use.

$HSCH_2CH_2OH$

12.47
2-Mercaptoethanol

CH_3COCH_2OH

12.48
Hydroxyacetone

Hydroxyacetone (12.48), originally introduced for vat dyeing, has proved moderately successful with sulphur dyes. This compound requires strongly alkaline conditions, the concentrations being critical. Colour yields are somewhat lower than with sulphide, the product is flammable and the dyebaths have an odour characteristic of acetone. Nevertheless, when used with CI Solubilised Sulphur dyes the effluent is free from sulphide. Mention has been made already of its possible use in a binary system with glucose [207]. Hydroxyacetone is the basis of the RD (Refine Dyeing) process of Ipose GmbH; this is a carefully optimised system incorporating automatic dosing of hydroxyacetone as the sole reducing agent [212]. Hydroxyacetone is suitable for application in indigo, vat and sulphur dyeing, including the continuous dyeing of cotton yarn with sulphur dyes or indigo, as well as the exhaust dyeing of knitgoods [212]. These processes are described in greater detail in section 12.9.

Thiourea dioxide, also discussed further in section 12.9, has been regarded as a more environmentally friendly replacement for sodium sulphide in the application of sulphur dyes [213]. In an investigation of exhaust dyeing with eight sulphur dyes applied from alkaline dyebaths, thiourea dioxide gave colour yields and fastness ratings similar to those with sodium sulphide, although in some cases slightly different hues were observed. Typical analyses of exhaust dyebaths are detailed in Table 12.28. On balance, thiourea dioxide is much less hazardous to the environment than sodium sulphide; the major improvement is the decreased amount of oxidant required for chemical treatment of the effluent and a second advantage is the marked decrease in sulphate ion content. Although thiourea

Table 12.28 Analysis of exhaust dyebaths after dyeing of cotton fabric with sulphur dyes using sodium sulphide or thiourea dioxide [213]

	3% CI Sulphur Yellow 1		10% CI Sulphur Blue 11	
	Sodium sulphide	Thiourea dioxide	Sodium sulphide	Thiourea dioxide
Colour	Yellow	Yellow	Blue	Blue
pH	10.2	11.4	11.2	9.1
Density at 20 °C (g/ml)	1.05	1.04	1.10	1.06
Permanganate oxidation (mg/l O_2)	937	433	1375	850
Dichromate oxidation (mg/l O_2)	1853	965	2769	1692
Residue dried at 100 °C (mg/l)	7720	6416	13500	8255
Residue baked at 600 °C (mg/l)	6612	4924	12495	7130
Loss of mass at 600 °C (mg/l)	1108	1492	1005	1125
Chloride (mg/l Cl^-)	Trace	Trace	Trace	Trace
Sulphate (mg/l $[SO_4]^{2-}$)	3439	933	5813	1382
Sulphide (mg/l $[S]^{2-}$)	128	Nil	72	Nil
Alkalinity (ml/l)	43	80	70	77

dioxide is more expensive, calculations of processing costs must take into consideration the cost of treating waste liquors compared with those containing sulphide.

Indirect electrolysis using regenerable redox systems, first proposed for use with vat dyes (section 12.9), can also be used with sulphur dyes [214]. Sulphur dyes develop a reduction potential of around –600 mV, compared with –900 mV for typical vat dyes (Ag/AgCl, 3M KCl). This is an important reason why a greater variety of reducing agents has been proposed for use with sulphur dyes compared with vat dyes. There are also wider possibilities for using various redox systems appropriate to the types of sulphur dye. Figure 12.21 shows the relationships between reduction potential and pH for vat, indigo and sulphur dyes, together with relevant redox systems. This indicates that anthraquinone derivatives and iron–gluconic acid complexes are suitable for the reduction of sulphur dyes by indirect electrolysis. Table 12.29 shows the important reaction paths involved in these two systems.

Representative anthraquinone compounds include alizarin (1,2–dihydroxyanthraquinone), sodium anthraquinone-2-sulphonate or disodium anthraquinone-1,5-disulphonate. Table 12.30 shows typical results obtained with various sulphur dye types. Schemes 12.10 and 12.13 represent generation of the reducing species at the cathode. Schemes 12.11 and 12.14 indicate the mechanism of reduction of water-insoluble CI Sulphur dyes, whilst Schemes 12.12 and 12.15 show the release of the water-soluble leuco species from the CI Solubilised Sulphur precursor. Schemes 12.16 and 12.17 represent undesirable problems of precipitation that can occur in some cases; these may be preventable by addition of a sequestering agent. Excellent results, equivalent to those of conventional processes, were obtained [214]. This process offers advantages in terms of savings of chemicals, regeneration of the reducing species *in situ*, no undesirable by-products from the reducing agent, as well as possibilities for dyebath recovery and effluent recycling.

Secondary auxiliaries used with the reducing system during preparation of the leuco dyebath may include wetting and sequestering agents; the water-insoluble CI Sulphur dyes may also require dispersing agents, The choice of wetting agent is not particularly critical as the behaviour of most sulphur dyes is unaffected apart from one or two that can show an

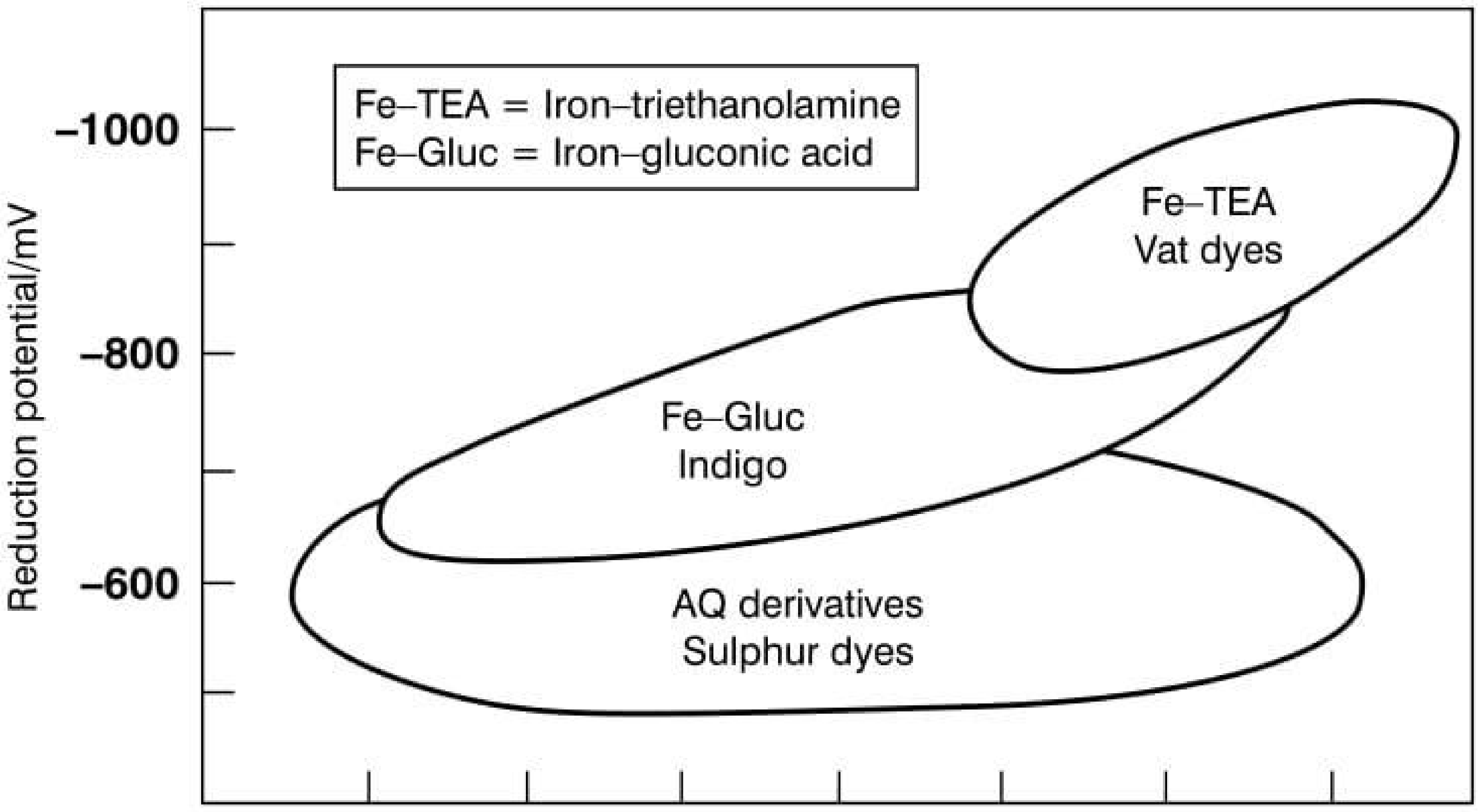


Figure 12.21 Relationships between reduction potential and pH for various redox systems and dye classes [214]

Table 12.29 Reaction paths involved in anthraquinonoid and iron-complex redox systems [214]

ANTHRAQUINONE SYSTEMS

Cathodic reduction of anthraquinone derivative
Scheme 12.10 $AQ + 2e^- \longrightarrow AQ^{2-}$

Reduction of water-insoluble CI Sulphur dye
Scheme 12.11 $R{-}S{-}S{-}R + AQ^{2-} \longrightarrow 2R{-}S^- + AQ$

Reduction of CI Solubilised Sulphur dye
Scheme 12.12 $2R{-}S{-}SO_3^- + AQ^{2-} \longrightarrow 2R{-}S^- + 2SO_3^{2-} + AQ$

IRON-COMPLEX SYSTEMS

Cathodic reduction of iron-complex system
Scheme 12.13 $Fe^{3+}L + e^- \longrightarrow Fe^{2+}L$

Reduction of water-insoluble CI Sulphur dye
Scheme 12.14 $R{-}S{-}S{-}R + 2Fe^{2+}L \longrightarrow 2R{-}S^- + 2Fe^{3+}L$

Reduction of CI Solubilised Sulphur dye
Scheme 12.15 $R{-}S{-}SO_3^- + 2Fe^{2+}L \longrightarrow R{-}S^- + SO_3^{2-} + 2Fe^{3+}L$

Precipitation of iron sulphides
Scheme 12.16 $Fe^{2+}L + 2Fe^{3+}L + 4S^{2-} \longrightarrow FeS\downarrow + Fe_2S_3\downarrow + 3L$

Precipitation of water-soluble leuco dye
Scheme 12.17 $Fe^{2+}L + Fe^{3+}L + 5R{-}S^- \longrightarrow (R{-}S)_2Fe\downarrow + (R{-}S)_3Fe\downarrow + 2L$

$R{-}S{-}S{-}R$	CI Sulphur dye	AQ	Anthraquinone derivative
$R{-}S{-}SO_3^-$	CI Solubilised Sulphur Dye	L	Ligand (gluconic acid or triethanolamine)

adverse reaction (lower yield or even precipitation) with certain nonionic surfactants. Suitable sequestering agents include sodium hexametaphosphate and EDTA [30]. Electrolytes are added to assist exhaustion in batchwise dyeing. After application of the leuco dyes a thorough rinse is essential to remove any loose dye from the fibre surface.

12.8.2 Oxidation

Chemically simple thiols and thiolates are readily oxidised to disulphides (Scheme 12.18). The situation is more complex with the leuco sulphur dyes [204]. In addition to having two or more thiol groups, they may contain other reactive functions that are potentially susceptible to oxidative attack, examples being primary, secondary or tertiary amino groups, hydroxy groups and aryl thioether (R–S–R) groups, as well as sulphonic acid groups in some cases. Furthermore, the high substantivity of the leuco dye for the substrate may inhibit free movement of the dye molecules and thus prevent complete conversion of thiol groups to

$$2\ R{-}SH \xrightarrow{\text{oxidant}} R{-}S{-}S{-}R$$

Scheme 12.18

Table 12.30 Suitability of various sulphur dye types for application with anthraquinonoid or iron-complex redox systems [214]

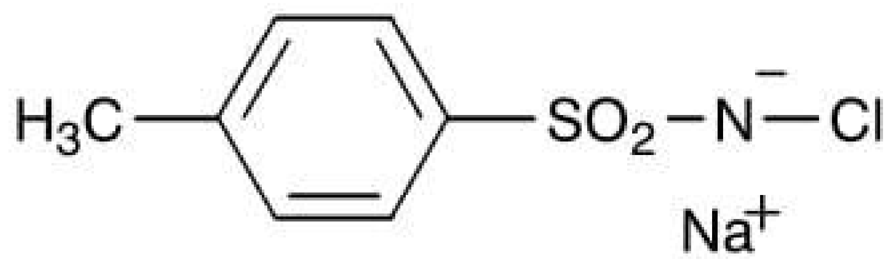
Sulphur dye types	AQ	Fe-GLU pH 12	Fe-GLU pH 13	Fe-TEA
Pre-reduced dyes				
CI Leuco Sulphur Black 1	+	o	–	+
CI Leuco Sulphur Black 2	+	o	–	+
Water-insoluble dyes				
CI Sulphur Blue 11	+	+	+	o
CI Sulphur Green 2	+	+	+	o
Water-soluble dyes				
CI Solubilised Sulphur Blue 7	+	+	+	o
CI Solubilised Sulphur Blue 10	+	+	+	o
CI Solubilised Sulphur Green 3	+	+	+	o
Sulphurised vat dyes				
Hydron Blue 3R Stabilosol (DyStar)	+	+	o	o
Hydron Blue R	+	+	–	o
Hydron Black CL	+	+	–	o
Hydron Red GGF	+	+	+	+

+	suitable
o	limited suitability
–	precipitation at high concn.
AQ	anthraquinonoid compounds
Fe-GLU	iron-gluconic acid complex
Fe-TEA	iron-triethanolamine complex

disulphide crosslinks; nevertheless, it is generally assumed that disulphide or polysulphide crosslinks are formed.

From a purely technical viewpoint, ignoring environmental concerns, the most favoured and most widely effective oxidising system for sulphur dyes is sodium dichromate acidified with acetic acid. The concentration of dichromate is not critical [30], 1–2 g/l being generally recommended for batchwise processes carried out at 60–80 °C, but the pH is more important and should be controlled to within the range 4.5–5.5, giving good colour yield and fastness properties more reliably than all other oxidising systems. Up to 1 g/l copper(II) sulphate may be added to dichromate baths to give an improvement in light fastness, at the expense of some dulling of shade and a harsher handle. The copper salt should only be added to acidified and sulphide-free liquors, otherwise it may precipitate as the hydroxide and/or sulphide. The addition of copper should not be made when oxidising sulphur blacks, however, since it promotes acid tendering with these dyes. The addition of sequestering and dispersing agents to the dichromate bath may give an improvement in fastness to rubbing [30].

Dichromate oxidation does tend to give a harsher handle and a less hydrophilic fibre, tending to cause handling problems in subsequent processes such as weaving, and is therefore less suitable for yarn dyeings. The technical merits of dichromate are overshadowed by ecological considerations, however, since chromium compounds in surface waters pose a direct threat to health and are increasingly restricted by water treatment



12.49

authorities. Hence oxidation by dichromate is now only carried out in certain regions of the developing world. Despite considerable efforts to develop alternatives, no system so far devised matches the versatility, efficacy, economy and reliability of acidified dichromate [30,202,204,210]. Oxidising agents that are increasingly used include (a) hydrogen peroxide or other peroxy compounds, (b) iodates or bromates, (c) sodium chlorite, or (d) sodium *N*-chloro-*p*-toluenesulphonamide (12.49). It has been reported [207] that classes (b) to (d) account for 70% of the market. However, all of these produce organic halogen compounds, giving rise to high AOX values in the effluent.

Air oxidation is obviously the most economical and environmentally friendly method but it has serious limitations. Peroxide systems are likely to become the most important method on both economic and ecological grounds, since peroxides do not generate AOX values. In fact peroxides are already established alternatives to dichromate, especially for yarn dyeing (giving a softer handle) and for sulphur blues and blacks. About 1–2 g/l hydrogen peroxide (130 vol.) is generally used at pH 10 and 40 °C [30,210]. Careful control is necessary, since under alkaline conditions oxidation is rapid and may go beyond the disulphide stage. In mildly acidic media oxidation is much slower but adequate under batchwise conditions for most dyes except CI Sulphur Red 10. It is too slow for rapid continuous methods and there is a danger of catalytic degradation of the fibre. Nevertheless, 1 g/l hydrogen peroxide (130 vol.) with 0.8 g/l acetic acid at 50–60 °C is widely used in yarn dyeing [30]. Oxidation under neutral conditions is occasionally carried out. Electronic metering and control is particularly useful with peroxide systems. The use of metal-ion catalysts with peroxide has been tried; vanadates offer some promise but iron and copper salts have not proved entirely suitable [210]. Peroxide oxidation has gained a reputation for giving somewhat lower fastness to washing than that obtained with dichromate. Although true in relation to traditional wash tests based on soap, tests based on the perborate-containing detergents in general use nowadays do not show this problem [210].

A concentration of 0.2–1.5 g/l potassium or sodium iodate [30,210] at 60 °C and pH 3.5–5 (preferably 3.5–4.0) gives similar hues and fastness properties to those obtained with dichromate. Although expensive, the process shows good reproducibility and does not give the harsh handle associated with dichromate. The pH, controlled using acetic acid, is critical; oxidation is slower at values higher than pH 4.5 and stronger acids such as formic acid lead to precipitation of iodine which is corrosive to machinery and environmentally harmful. Higher temperatures lead to partial reduction of the iodate with consequent loss of efficacy. Under the same conditions bromates are less effective than iodates but perform equally well if a catalyst such as sodium metavanadate ($NaVO_3$) is added [30]. Metavanadate, however, is increasingly under environmental scrutiny.

Sodium chlorite is the basis of several proprietary oxidising agents for sulphur dyes. It is used at pH 10 (sodium carbonate) and 90–95 °C; careful control of conditions is important as the reaction is rather slow. The presence of additives is necessary for the successful use of chlorite. The proprietary formulations contain stabilisers, EDTA-type sequestering agents and detergents or dispersing agents. Other oxidising agents that have been proposed include:

(1) Sodium *m*-nitrobenzenesulphonate in alkaline media
(2) Sodium salt of *N*-chloro-*p*-toluenesulphonamide (12.49; chloramine T)
(3) Sodium nitrite with sulphuric acid (this carries a danger of fibre degradation)
(4) Potassium or ammonium salts of peroxydisulphonic acid with acetic acid.

12.8.3 Alkylation of thiol groups and other aftertreatments

As an alternative or supplement to oxidising treatments, many leuco sulphur dyeings can be treated with alkylating agents such as those based on epichlorohydrin. This was discussed in section 10.9.6. The alkylating agent reacts with the dye thiol to yield an alkyl thioether, or with amino groups in the dye to yield substituted amines [204]. These are generally referred to as fixation treatments and give enhanced fastness to acid storage and to wet treatments although, strictly speaking, they are still oxidation mechanisms involving the removal of an electron from the dye thiolate. Several commercial cationic fixing agents for direct dyeings can be used to aftertreat sulphur dyeings, giving enhanced wet fastness; these treatments are claimed to be effective if applied in place of oxidation [215–217]. A soaping treatment after oxidation or other fixation treatment is recommended.

12.8.4 Continuous dyeing

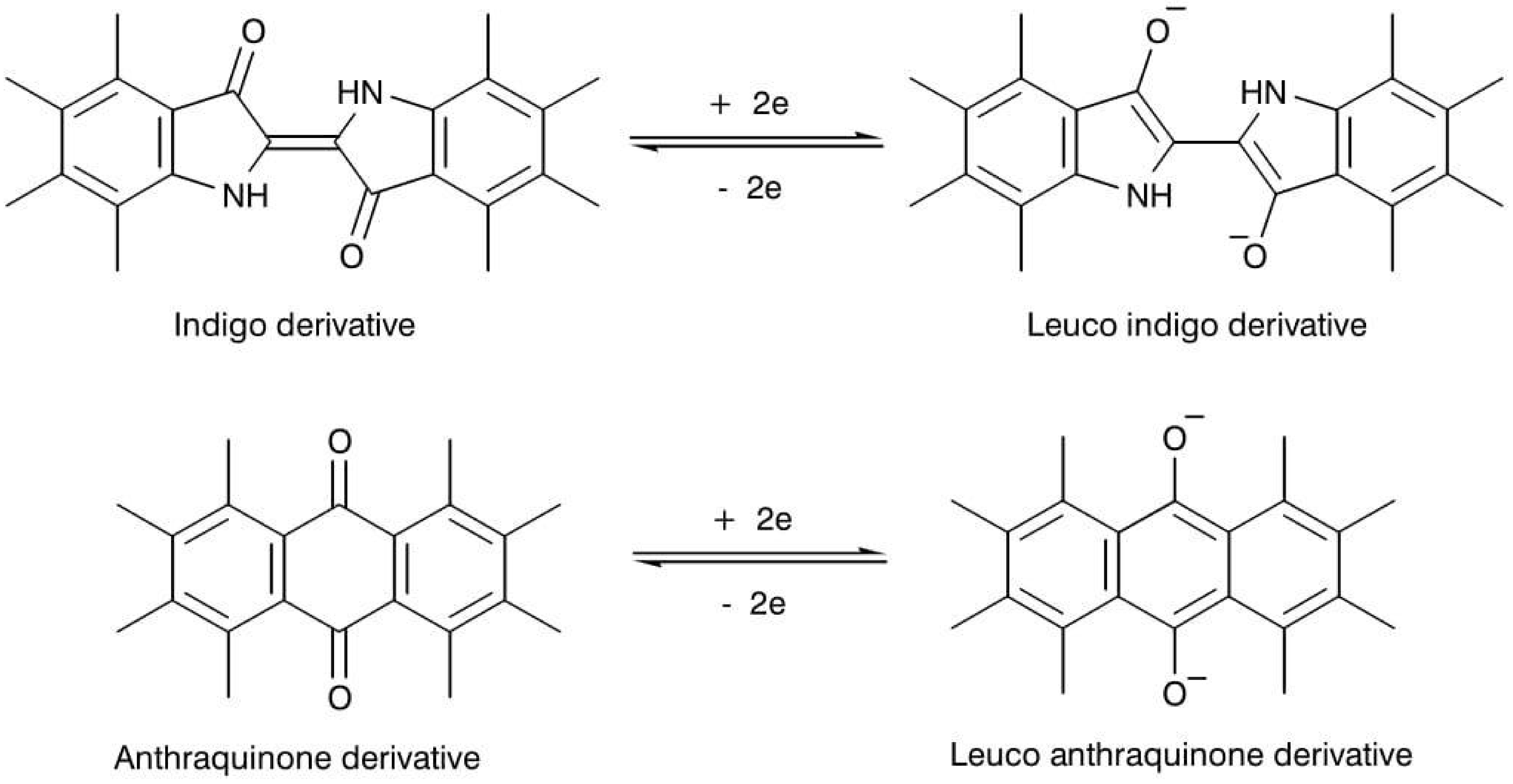
Continuous methods are far more important with sulphur dyes than is batchwise dyeing in terms of production volumes. There are many methods, including pad–steam, pad–sky, pad–dry–chemical–pad–steam and pad–dry–develop; summary descriptions of these processes are available [30]. In general the auxiliaries used, and particularly the redox chemicals, are the same as those used in batchwise dyeing although they are usually used in higher concentrations, especially reducing agents because they are more exposed to air in continuous processes. Wetting and sequestering agents are generally used. Some processes incorporate hydrotropes (such as urea) and migration inhibitors. Electrolytes may be used in a chemical (reducing) pad to assist fixation but are less frequently used when padding with leuco dyes, since they can promote tailing effects.

12.9 VAT DYES

Vat dyes, like sulphur dyes, are applied to cellulosic fibres after initial conversion by alkaline reduction to the substantive leuco form, followed by reoxidation to the insoluble form on the fibre. Consequently the major auxiliaries are, once again, reducing and oxidising agents. Ancillary products include electrolyte, wetting, dispersing, levelling and sequestering agents; thickening agents and hydrotropes may feature in continuous dyeing and printing. An extremely important part of vat dye application is the final soaping treatment, which is essential for developing the ultimate colour and optimal fastness. Detailed accounts of vat dye application are available [30,218]. Here the reducing and oxidising stages of the process and the soaping treatment are considered separately; the main discussion deals with batchwise dyeing, after which the requirements for continuous dyeing and printing are considered.

12.9.1 Reduction

Vat dyes are available mainly in their water-insoluble pigment form, although a group of solubilised dyes, the vat leuco esters, are supplied in a stabilised pre-reduced form that does not require any reduction by the dyer. The chemistry of vat dyes, and of their reduction and oxidation, is much more clearly understood than is the case with sulphur dyes. In essence, the reduction process can be represented as the addition of an electron to each of the keto groups of the vat dye, with conversion to a conjugated dihydric quinol, the system being readily reversible by oxidative abstraction of electrons (Scheme 12.19). Vat dyes generally have larger negative reduction potentials than sulphur dyes and so require more strongly reducing conditions. In a detailed account of reduction and oxidation processes [219], various vat dyes are shown to have reduction potentials in aqueous media varying from –770 to –1000 mV, the majority being in the region –900 to –950. In contrast, sulphur dyes average only about –600 mV. Published reduction potentials for various reducing agents in aqueous alkaline media are shown in Table 12.31.



Scheme 12.19

Table 12.31 Reduction potentials of various reducing agents measured as 5 g/l solutions in 15 ml/l caustic soda 38°Be at 60 °C [220]

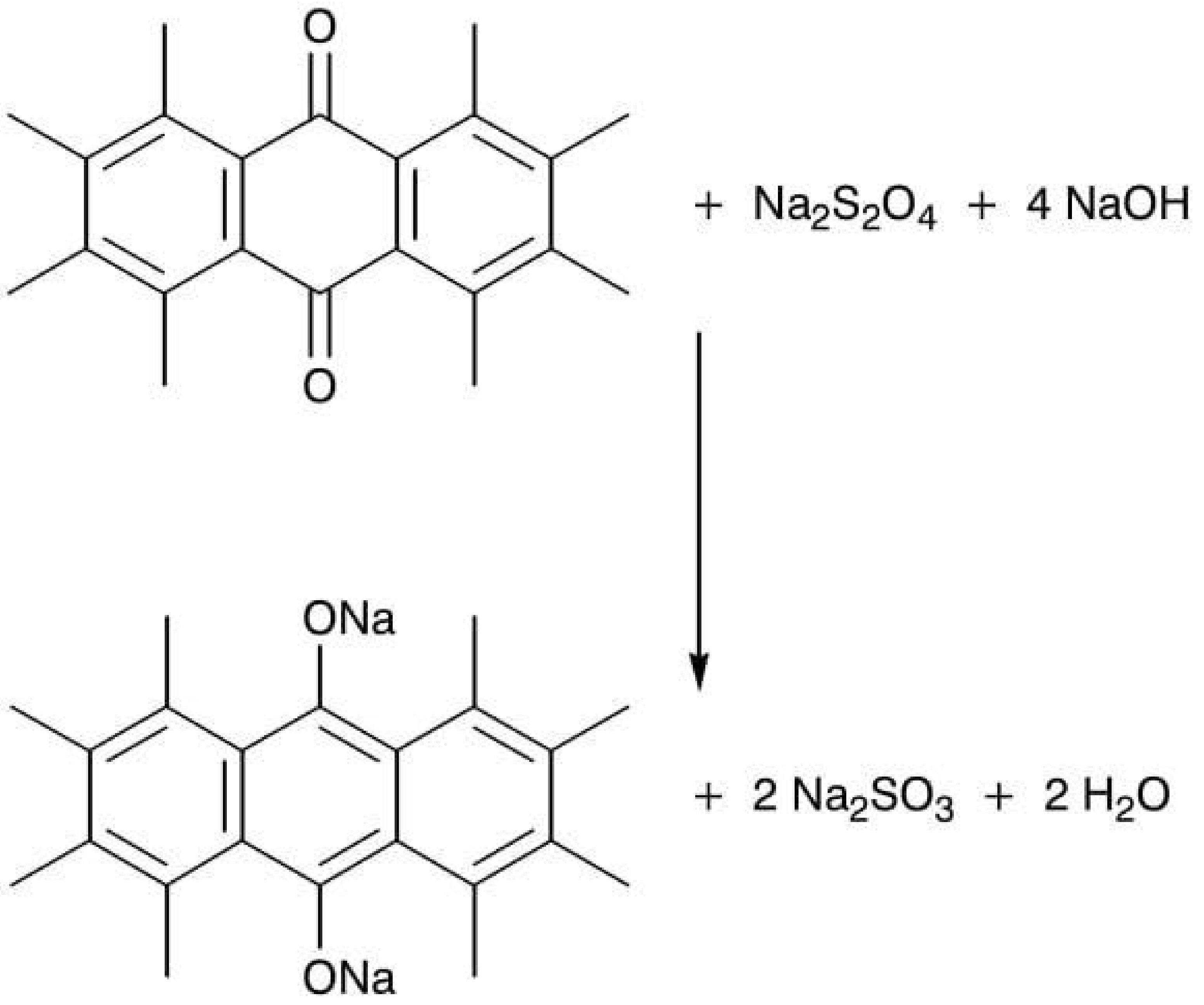
	Reduction potential (mV)
Thiourea dioxide	–1100
Sodium borohydride	–1100
Sodium dithionite	–970
Hydroxyacetone	–810
Sodium formaldehyde-sulphoxylate	–790

Alkali is an essential component of the reducing system in order to ensure that the substantive ionised leuco species is formed, since the acid leuco form is usually insoluble in water and has limited substantivity for cellulose. To be successful a reducing agent should have a lower reduction potential than the compound it is intended to reduce but in practice there are a number of complicating factors. For example, the reduction rate of a vat dye (section 3.1.4) is critically dependent on the physical form of the dye as characterised by its crystal form and particle size distribution [221,222]. Table 12.32 indicates the magnitude of this effect for various samples of CI Vat Green 1. The stability of the leuco dye in solution is a function of the concentrations of dye and reducing agent, temperature, pH and liquor ratio. The influence of oxidation in air as it relates to different application systems has to be carefully considered. Hence the quantities of reagents suggested by the dye manufacturers can only be used as preliminary guidelines.

By far the most important reducing system for the batchwise application of vat dyes is sodium dithionite ($Na_2S_2O_4$) in a solution of sodium hydroxide. Obviously the theoretical concentrations required will depend on the number of keto groups in the dye molecule and on its relative molecular mass and concentration, but the reaction can be represented as in Scheme 12.20 for an anthraquinonoid dye with two keto groups. The effect of air oxidation on alkaline

Table 12.32 Effect of particle size on rate of reduction of CI Vat Green 1 at 20 °C [221]

Percentage of dye particles >1.05 μm	Time (min) to reduce 50% of the dye
66	206
42	120
22	70
6	42
2	28
1	7
CI Vat Green 1 (23%)	100 mg/l
Sodium dithionite	5 g/l
Caustic soda 38°Be	10 g/l



Scheme 12.20

$$Na_2S_2O_4 + 2\,NaOH + O_2 \longrightarrow Na_2SO_3 + Na_2SO_4 + H_2O$$

Scheme 12.21

dithionite must also be taken into account in practical situations and this can be represented by Scheme 12.21 [30]. In practice, more sulphite than sulphate tends to be formed. Clearly, this atmospheric oxidation results not only in loss of reducing agent but also of alkali, another reason why excess alkali as well as reducing agent is required. The influence of atmospheric oxidation varies enormously. Stability may be maintained for several hours in a large dyeing vessel providing the surface area of the liquor is relatively small, compared with only 30–60 seconds in a padding system.

The ideal pH value for this system is between 12 and 13; below pH 12 there is an increasing danger that the dye will either revert to its keto form or yield the leuco acid, whereas above pH 13 there is a danger that the dithionite may decompose to form thiosulphate, sulphite or even sulphide if the temperature is high enough. Specifically in the case of indigo, however, better reproducibility is achieved when buffered to pH 10.6–11.4 [223], rather than the traditional application conditions of pH 12.1–12.9. Mention has been made above of the need to have both dithionite and alkali present to excess in most dyeing systems. Unfortunately this has often led to the indiscriminate use of these chemicals, particularly of dithionite, resulting in high chemical costs and excessive contamination of the effluent. Providing suitable analytical monitoring is available, cost savings up to 40% are achievable if the quantitative amount of dithionite is present in the system [224]. Automatic dosing systems can result in both cost savings and improved quality. This is exemplified in Figure 12.22, which indicates that the conventional process of topping up at each end in jig dyeing results in a fluctuating dithionite concentration, whereas automatic dosing enables the required minimum concentration of dithionite to be constantly maintained.

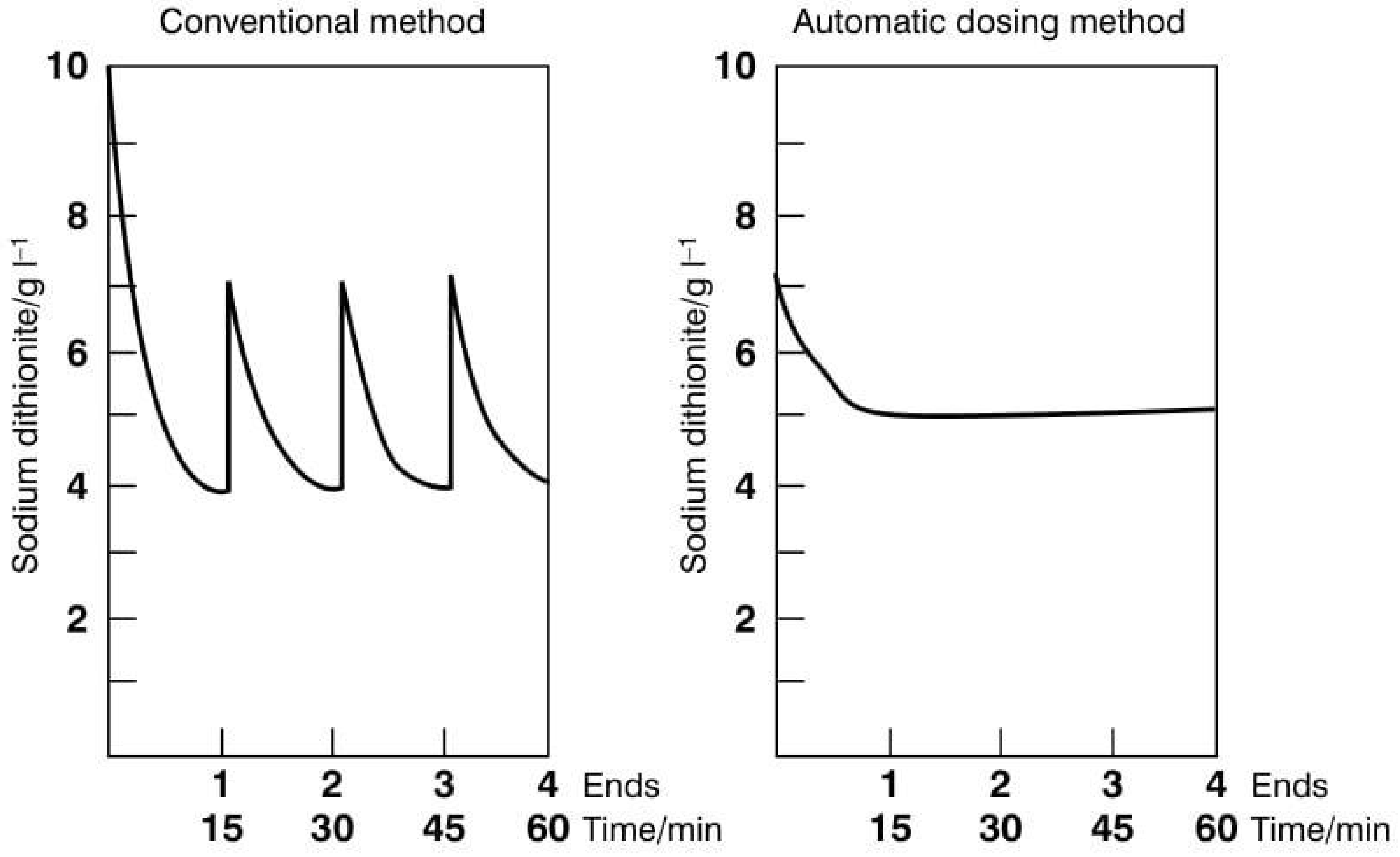


Figure 12.22 Variations in the concentration of sodium dithionite in jig dyeing using conventional and automatic dosing methods [225]

Table 12.33 Classification of vat dyes and chemical requirements

Group	Characteristics
IK	Relatively low substantivity for cellulose. Dyed at ambient temperature with a small amount of caustic soda and a high salt concentration.
IW	Higher substantivity for cellulose. Dye at 45–50 °C with more caustic soda and less salt (none for mercerised cotton or regenerated cellulosic fibres).
IN	Much higher substantivity for cellulose. Dyed at 60 °C with even more caustic soda but without salt.
IN Special	High substantivity and the maximum alkali concentration.

Table 12.34 Guideline chemical concentrations for 2% o.w.f. vat dye at 10:1 liquor ratio [226]

Dye group	Temperature (°C)	Caustic soda (g/l)	Sodium dithionite (g/l)	Sodium sulphate (g/l)
IK	20–25	3.6	3.0	12.0
IW	45–50	4.8	4.0	12.0
IN	60	8.8	5.0	–

Electrolyte is sometimes used in the application of vat dyes from alkaline dithionite dyebaths. The quantities of chemicals required vary according to conditions and dye manufacturers' literature should be carefully consulted, supplemented by local knowledge based on experience. Vat dyes are generally classified into several groups (Table 12.33). Guideline recommendations for IK, IW and IN dyes applied from a 10:1 liquor are given in Table 12.34. Another source [30] indicates typical amounts as varying from:

5 ml/l	Caustic soda 27% (1.35 g/l NaOH)
2 g/l	Sodium dithionite

for pale depths of 1K dyes at 20:1 to:

25 ml/l	Caustic soda 27% (6.75 g/l NaOH)
7 g/l	Sodium dithionite

for full depths of IN dyes at 10:1

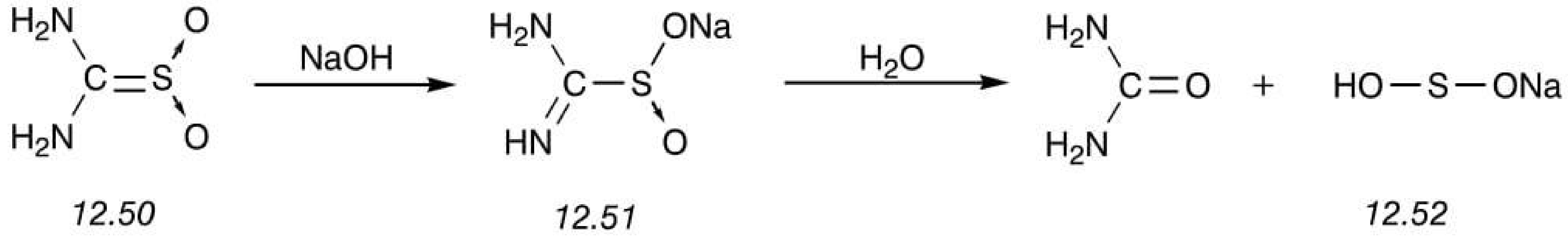
Higher dyeing temperatures (up to 115 °C) are selected in some cases. These conditions require a more stable reducing agent of the hydroxyalkylsulphinate type, typical concentrations being 10–20 ml/l caustic soda 27% and 5–10 g/l reducing agent according to dye concentration, liquor ratio and temperature. A reduction inhibitor, such as glucose, may be added when applying dyes that are sensitive to over-reduction [30]. In the so-called pigmentation process, the finely dispersed vat pigments are first applied at 60–80 °C, usually with addition of electrolyte, followed by reduction to the vat leuco form using dithionite and alkali.

The stability and efficacy of sodium dithionite can be enhanced by addition of polyacrylamide, a product more frequently used as a migration inhibitor in continuous dyeing processes [227]. This biodegradable polymer allows the amount of dithionite to be decreased, giving improved fixation with less contamination of effluent by dye and dithionite. In jig dyeing polyacrylamide helps to prevent oxidation spots and minimises end-to-end and side-to-side variations.

There are potential environmental problems associated with sodium dithionite, since in effluent it can produce sulphite and sulphate. Although the sulphite can be oxidised quite easily to sulphate, this does not entirely obviate the problems since high concentrations of sulphate can cause damage to unprotected concrete pipes. Thus there are environmental reasons for alternative reducing agents to dithionite and several are available, although mainly used for special purposes. In particular, their greater stability to atmospheric oxidation makes them of special interest for continuous dyeing and printing processes, rather than for batchwise dyeing.

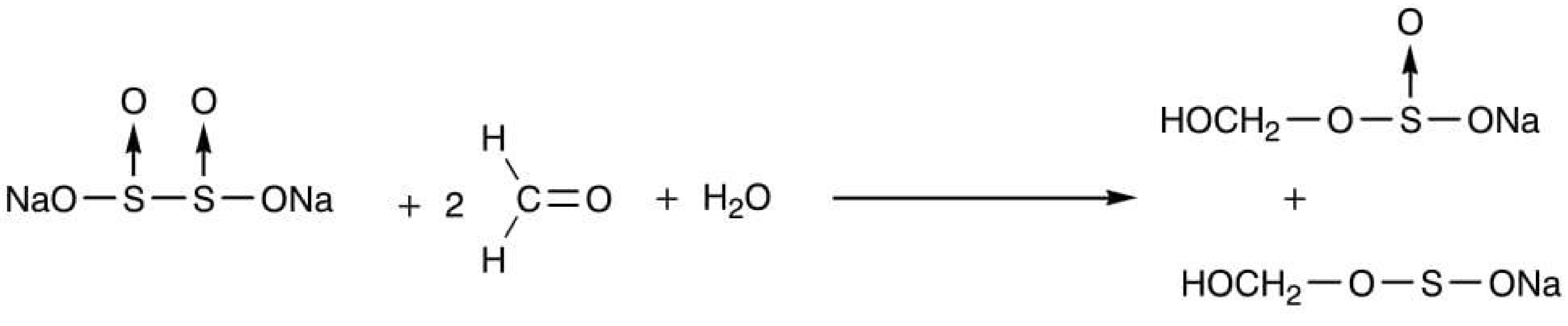
Thiourea dioxide (12.50) or formamidinesulphinic acid is a powerful reducing agent for vat dyes. This compound has a lower relative molecular mass than sodium dithionite and gives lower concentrations of sulphite and sulphate in the effluent, but shows certain disadvantages. The mode of action in hot aqueous alkali is represented in Scheme 12.22, showing first the rearrangement to sodium formamidinesulphinate (12.51), which then decomposes to yield urea and the active reducing species, sodium hydrogen sulphoxylate (12.52). Although thiourea dioxide is more stable than dithionic acid, the formamidinesulphinate formed in alkaline media is more readily oxidised than dithionite, thus negating any potential advantages. This agent can cause over-reduction of indanthrone vat dyes, against which inhibitors such as glucose or sodium nitrite have no palliative effect. Experimental work has indicated the possibility of using thiourea dioxide in combination with other compounds such as (a) sodium dithionite, formaldehyde and sodium hydroxide, or (b) saturated aliphatic ketones, but commercial exploitation has not been evident [218].

Greater commercial significance is attached to certain derivatives of sodium dithionite, including sodium formaldehyde-sulphoxylate (12.53; hydroxymethanesulphinate) (Scheme 12.23) and the less important sodium acetaldehyde-sulphoxylate (12.54; hydroxyethanesulphinate). These reducing agents have been of particular interest in printing, especially in the flash-ageing process [228–231]. The formation of sodium formaldehyde-sulphoxylate by reaction of sodium dithionite with formaldehyde is shown in Scheme 12.23; the bisulphite formed can be further reduced with zinc to produce another molecule of the sulphoxylate.



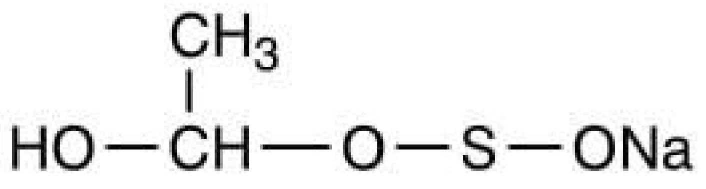
12.50 12.51 12.52

Scheme 12.22



12.53

Scheme 12.23



$HO-CH(CH_3)-O-S-ONa$

12.54

$HOCH_2-O-S-OZn(OH)$

12.55

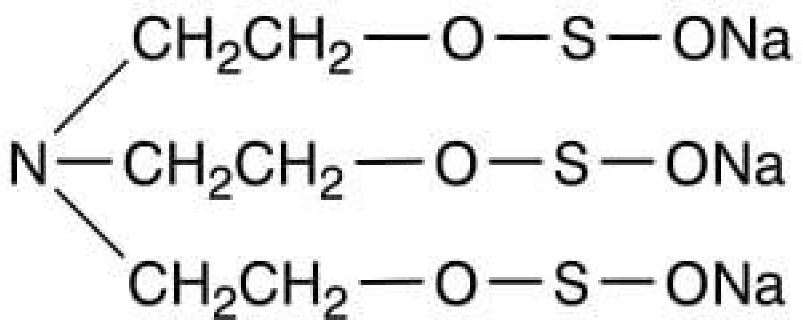
$HOCH_2-O-S-OCa(OH)$

12.56

These reducing agents are much more stable than sodium dithionite at lower temperatures; hence they can be used to prepare stable pad liquors and print pastes. At higher temperatures, as in steam fixation treatments, they are capable of bringing about rapid reduction of vat dyes. Sodium formaldehyde-sulphoxylate was used first in conventional steam fixation of vat prints, although the acetaldehyde analogue was initially preferred for the flash-ageing process. As vat dyes are invariably fixed under alkaline conditions, the sodium salts of the sulphoxylates are preferred to the basic salts of zinc (12.55) or calcium (12.56), which are unstable under alkaline conditions.

Sodium formaldehyde-sulphoxylate has been used occasionally in combination with sodium dithionite [218) but other two-component or two-phase systems based on formaldehyde-sulphoxylates have generally depended on an accelerating or catalyst system. For example, a process that has been adopted to some extent in bulk practice [232,233] comprises a strongly alkaline solution of sodium borohydride (12.57; sodium tetrahydroborate), together with a second reducing system consisting of sodium formaldehyde-sulphoxylate and the catalyst sodium nickel cyanide. Various advantages have been claimed for this process, although there are misgivings regarding the environmental acceptability of sodium nickel cyanide [234]. Other accelerators used with sodium formaldehyde-sulphoxylate include sodium dimethylglyoxime complexes, anthraquinone and aminoanthraquinonesulphonic acids. Although sodium borohydride is itself a reducing agent, it generally reacts too slowly alone for use in vat systems; nor is there any evidence that it will act as a stabiliser for sodium dithionite [235], as has sometimes been suggested. Another reducing agent, suggested [236] for both flash-age printing and batchwise high-temperature package dyeing, is trisodium nitrilotriethanesulphinate (12.58). This does not appear to have attained commercial use, however.

12.57 $NaBH_4$



12.58

Hydroxyacetone (12.48), mentioned in section 12.8.1 in connection with sulphur dyes, is sulphur-free and biodegradable. This compound was originally proposed for use with vat dyes and continues to generate some interest. This agent can be used for the pad–steam application of vat dyes in the presence of high concentrations of sodium hydroxide (about 3.5–4.5 g/l). Hydroxyacetone does not cause over-reduction of indanthrone vat dyes but does give different shades with carbazole dyes, compared with sodium dithionite [218].

The optimised and metered use of this product is central to the RD (Refine Dyeing) process of Ipose GmbH [212]. This process, for which both environmental and economic advantages are claimed, is suitable for applying indigo on continuous yarn-dyeing ranges and for knitgoods dyeing with vat dyes that are difficult to reduce. Although colour yields are not quite as high as with dithionite, the advantages include biodegradability, decreased chemical usage, lower COD values and the effluent contains no sulphide, sulphite or sulphate. This process depends on optimal machinery technology coupled with optimised computer-controlled chemical dosing. Specific advantages in continuous yarn dyeing with indigo include [212]:

(1) high quality with a good ring-dyeing effect, a prime requirement in indigo warp dyeing for denim jeans
(2) greater elasticity of yarn with fewer yarn breaks and therefore higher productivity
(3) higher dye exhaustion and thus less residual dye in the effluent
(4) lower chemical usage and thus 20% less waste liquor
(5) liquid form of indigo for ease of application
(6) minimal effluent problems as only biocompatible chemicals are used, with possibilities for recycling of liquors and recovery of dye through ultrafiltration
(7) no health hazard nor odour of hydrogen sulphide.

Typical waste water analyses and relative costings for sodium dithionite and hydroxyacetone are given in Table 12.35.

Table 12.35 Continuous dyeing of cotton yarn with indigo using sodium dithionite or hydroxyacetone [212]

Waste water analysis	Sodium dithionite	Hydroxyacetone
Dye (g/l)	1.5	0
Sulphide (mg/l)	12.5	1
Sulphite (mg/l)	64	1
Sulphate (g/l)	19	0.2
Phosphate (mg/l)	60	6
*COD (mg/l)	7000–8000	700–1000
Surfactant (mg/l)	18–19	1.5
Sequestering agent (mg/l)	6	0
Dye and chemical cost	100%	77%
Productivity	100%	140%

* COD values for hydroxyacetone are after treatment in a bioreactor; such treatment is not possible with dithionite.

Tests using indigo have shown that reduction with alkaline hydroxyacetone is most reproducible when the concentrations are as follows [237]:

Hydroxyacetone	5.0–12.5 ml/l or 0.054–0.135 mol/l
Sodium hydroxide	5.0–12.5 g/l or 0.125–0.312 mol/l

It is interesting to note that the rate of vatting of indigo with hydroxyacetone under these conditions can be increased approximately fourfold using ultrasound, as illustrated in Figure 12.23. The ultrasound causes cavitation in the indigo pigment dispersion, accelerating the disintegration of the insoluble dye particles and thus increasing the probability of collisions between reducing agent and dye molecules.

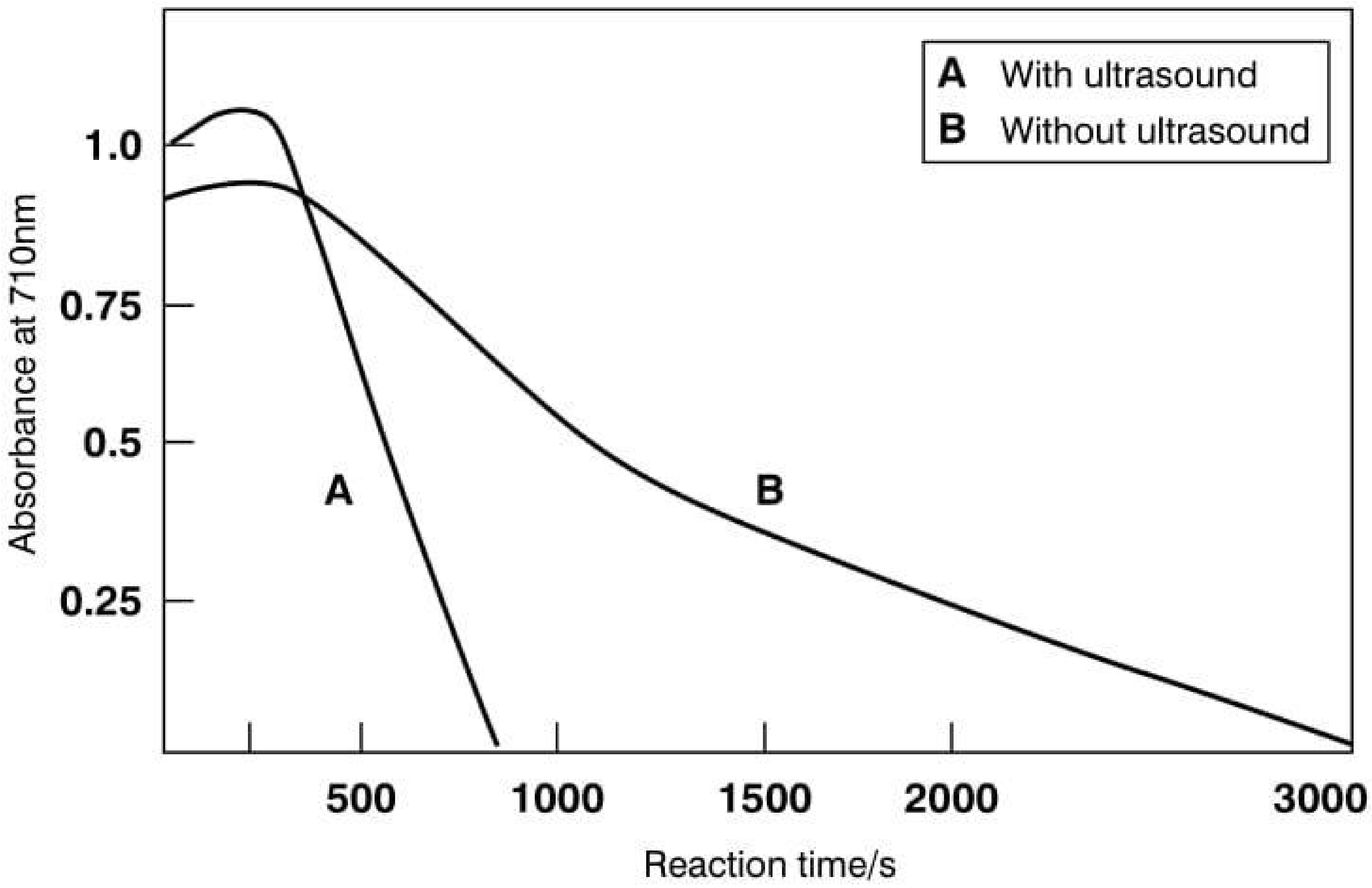


Figure 12.23 Rate of reduction of indigo with and without ultrasound [237]. 0.1 g/l Indigo, 40 °C; 2.5 ml/l hydroxyacetone; 5.0 g/l sodium hydroxide, pH 12.7; 0.03 g/l anionic dispersing agent

Iron complexes have been investigated as alternatives to sodium dithionite in vat dyeing [238]. Iron(II) hydroxide $Fe(OH)_2$ is a powerful reducing agent and this reducing power increases with increasing alkalinity of the medium. Alkalinity results in precipitation, however, and the hydroxide must be converted to a complex in order to maintain solution. The complex must be chosen to be reasonably stable, but not so inert that the iron(II) ion cannot exert its reducing action. Complexes with triethanolamine or gluconic acid are suitable, the latter being favoured on environmental grounds because it does not contain nitrogen. Investigation at a liquor ratio of 10:1 showed 50 ml/l caustic soda 38°Bé to be optimum, lower concentrations of alkali producing duller and weaker dyeings.

The molar ratio of iron(II) ion to gluconic acid in the complex prepared by reacting iron(II) chloride tetrahydrate with gluconic acid was significant. Less reducing agent was required for vat dye reduction at a molar ratio of 1:2 than at 1:1 but too low a concentration of iron(II) ions resulted in paler and unlevel dyeings because of insufficient vatting of the dye pigment. It is environmentally advantageous to keep the gluconic acid concentration low to ensure a low COD value. A 1:1 molar ratio is probably the optimum. The formation of iron(III) ions lowers colour yield but levelness is not affected because the gluconic acid holds the iron(III) ions in solution. The use of iron(II)-gluconic acid did not cause over-reduction of sensitive dyes even when dyeing was prolonged. With most dyes the colour yield was equal to that given by sodium dithionite. Precipitation of iron(III) hydroxide facilitates the elimination of dyes and auxiliaries from effluent after only a brief settlement time.

The application of indirect electrolysis in conjunction with regenerable redox systems, already described in section 12.8.1 for sulphur dyeing, has attracted considerable research interest for the reduction of vat dyes [239–241]. In environmental terms, the advantages of this system for vat dyeing would be similar to those for sulphur dyeing. Figure 12.21 and Table 12.29 are essential to an understanding of the physico-chemical aspects of the process. The reduction potentials attainable with anthraquinone derivatives as mediators of the redox system are shown in Table 12.36. In general, these potentials are too low for vat dyes, as can be seen by reference to Figure 12.21.

Table 12.36 Peak cathodic potentials of anthraquinone derivatives measured using Ag/AgCl/3M KCl in 4 g/l sodium hydroxide solution [239]

Anthraquinone derivative	Cathodic potential (mV)
1,2,5,8-Tetrahydroxy	–885
1,2-Dihydroxy (alizarin)	–880
1,8-Dihydroxy (chrysazin)	–770
1,4-Dihydroxy (quinizarin)	–760
1,2-Dihydroxy-3-sulphonic acid	–760
2-Sulphonic acid (β acid)	–750
1,5-Disulphonic acid	–750
1-Amino-2-carboxylic acid	–750
1-Amino-2-sulphonic acid	–720
2,6-Disulphonic acid	–560

Currently the most suitable system, that will generate potentials up to –1050 mV, is the iron-triethanolamine complex prepared from either iron(II) or iron(III) salts. Using iron(III) sulphate penta- or hexahydrate, for example, dyebaths are prepared by first dissolving sodium hydroxide in a small amount of water, to which is added the triethanolamine. Hydrated iron(III) sulphate is separately dissolved in a small amount of water and then added to the alkaline triethanolamine solution until the initially precipitated iron(III) hydroxide redissolves, after which the solution is diluted to full volume to give:

	g/l	mol/l
Sodium hydroxide	20	0.5
Triethanolamine	60	0.45
Hydrated iron(III) sulphate	14	0.027

A schematic illustration of this process is shown in Figure 12.24.

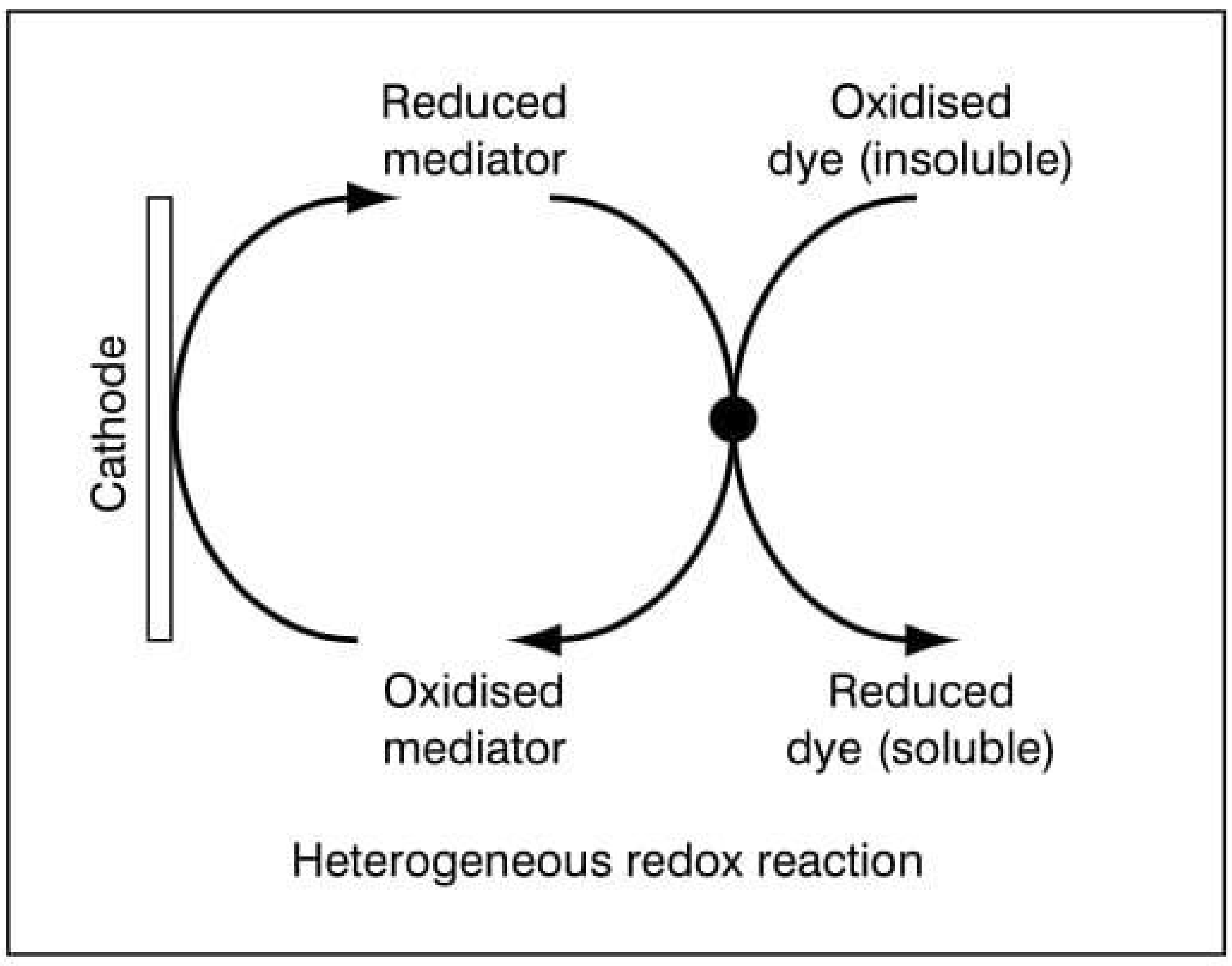


Figure 12.24 Schematic diagram of the cathodic reduction of the mediator that converts the insoluble vat dye into its soluble leuco form [239]

The essence of the technique is as follows [239]. The cathode reduces the mediator which then reduces the dye. This mediator (the regenerable redox system) must continually produce a consistent reduction potential in the dye liquor, so that no reducing agent has to be added. The prevailing potential is defined by the Nernst Equation (12.2):

$$\text{Redox pair: Oxi} + n\text{e}^- \rightleftharpoons \text{Red}^{n-} \qquad (12.1)$$

$$\text{E} = \text{E}^\circ + \frac{\text{RT}}{n\text{F}} \times \ln\frac{[\text{Oxi}]}{[\text{Red}]} \qquad (12.2)$$

E° = standard potential (mV) of the redox pair (under the experimental conditions)
E = potential (mV) prevailing in the solution
R = molar gas constant (8.314 J/°K.mol)
T = absolute temperature (°K)
F = Faraday constant (96 500 coulombs)
[Oxi] = concentration (mol/l) of the oxidised form of the redox pair
[Red] = concentration (mol/l) of the reduced form of the redox pair
n = electrochemical valency.

If the concentrations [Oxi] and [Red] are identical, the potential prevailing in solution is identical to the standard potential E° of the redox pair under the conditions of use. If the ratio of these concentrations [Oxi]/[Red] is modified by electrolysis, the potential changes accordingly:
if [Oxi] > [Red], E becomes positive and the action is one of oxidation
if [Oxi] < [Red], E becomes negative and the action is one of reduction

With conventional reducing agents the ratio [Oxi]/[Red] is determined by the decreasing concentration of reducing agent and the increasing concentration of oxidation products resulting from its decomposition. In an electrolytic process, however, this ratio can be adjusted so as to continually regenerate the redox pair and no secondary products are formed in the dye liquor, nor is there a build-up of unwanted oxidation products. After dyeing, the residual leuco dye can be reoxidised in the exhaust dyebath and removed by filtration; thus the dye liquor together with the mediator can be used several times, creating considerable ecological advantages. The requirements of a mediator or redox catalyst system are:

(1) only a small loss (if any) in activity during useful life; therefore the maximum possible number of reaction cycles
(2) rapid conversion at the electrode surface
(3) no catalysis of side reactions or changes in colour
(4) no affinity for the fibre
(5) no reaction with the solvent
(6) adequate solubility
(7) non-toxic
(8) no problems in effluent treatment
(9) inexpensive.

A more detailed overview of the process is shown in Figure 12.25, highlighting the main steps of a vat dyeing process. The quotient of a pair of k values (rate constants) for a reaction in the forward and reverse directions is a measure of the equilibrium constant of the reaction step. The reduction of the suspended oxidised form of the dye is characterised by the pair of rate constants, k_1 for reduction and k_2 for reoxidation. For effective vatting of the dye to be achieved, k_1 should be greater than k_2. A measure of the affinity of the reduced dye is given by the quotient of k_3 and k_4; a high value of k_3/k_4 is characteristic of dyes with good affinity for cellulosic fibres in their reduced form, leading to a high degree of dye exhaustion. This can cause problems in the dyehouse resulting from rapid exhaustion of the dyebath. The quotient k_8/k_7 describes the stabilisation of the reduced form of the dye adsorbed on the fibre. A high k_8/k_7 quotient indicates that the adsorbed leuco dye remains stable in its reduced form, an important precondition in achieving equilibrium during exhaustion of the dyebath. When the quotients k_1/k_2 or k_8/k_7 are small, the dyeing process is disrupted by all oxidising agents, including air, leading to unlevelness in the dyeing. It is evident that the rates of dye reduction (k_1 and k_8) are of great importance in ensuring reproducibility of dyeing. The rate of reduction achieved by the iron(II)-triethanolamine complex is several orders of magnitude greater than that given by sodium dithionite; therefore the reduced leuco dye is effectively stabilised and the resulting dyeings are more reproducible in the case of electrochemical reduction.

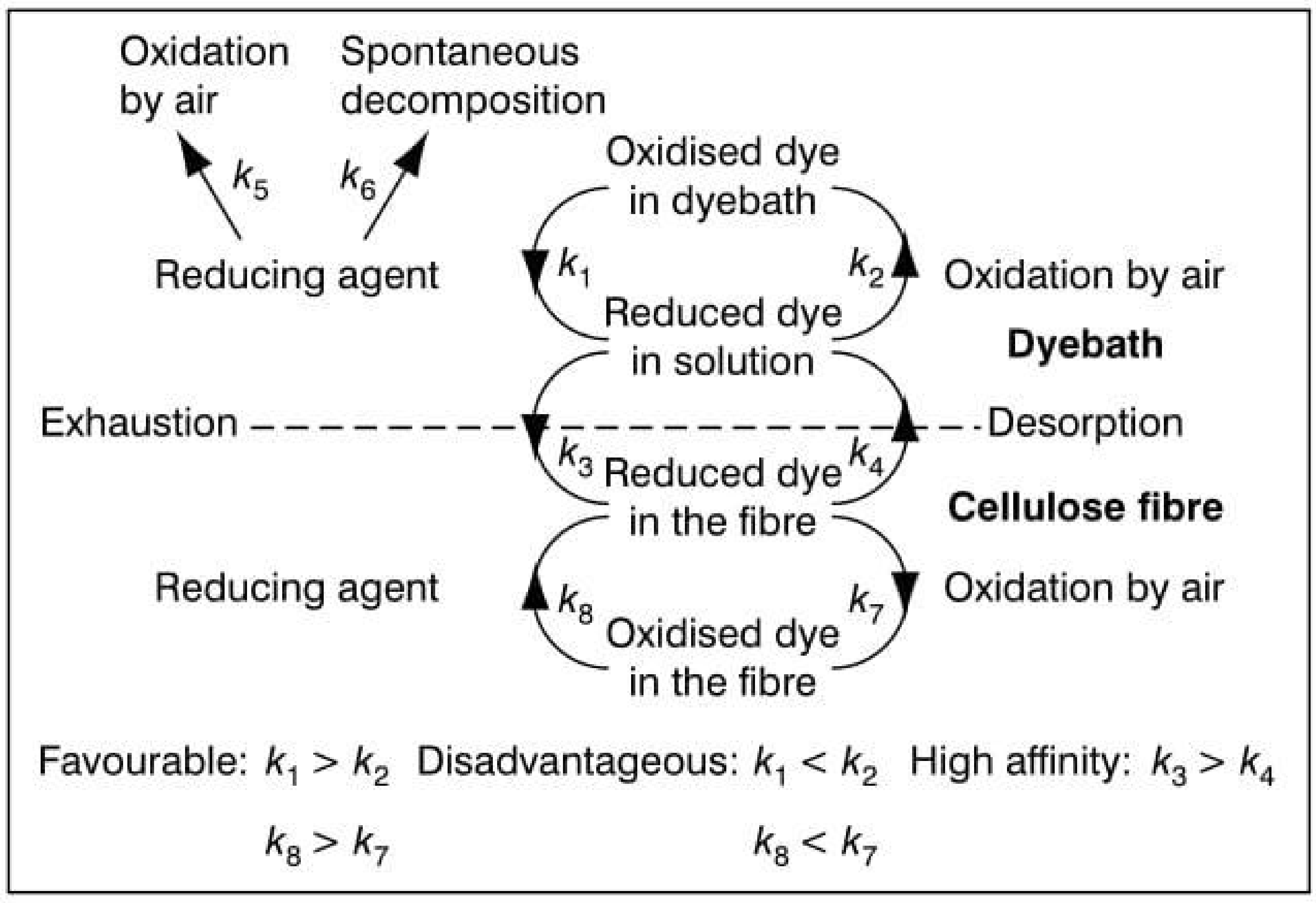


Figure 12.25 Reaction scheme of the steps occurring in a vat dye reduction process [240]

The special requirements of the indigo dyeing of cotton warp yarns for denim are capable of being met by indirect electrolysis systems [241]. Examples of four suitable redox systems are shown in Table 12.37. Uniform build-up of depth was observed with each successive step, the results being at least equal to those from the conventional dithionite-based process. Apparently these processes are amenable to scaling up to bulk production levels [241].

In spite of the many reducing systems evaluated or proposed (often quite convincingly), sodium dithionite remains the agent almost universally preferred [242]; others such as thiourea dioxide, sulphinates and hydroxyacetone are only used for special purposes. The advantages and disadvantages of the most important reducing agents are summarised in Table 12.38.

It is now opportune to consider additives for reduction systems. As mentioned above, the reduction process is invariably carried out in an alkaline medium, the most common alkali being sodium hydroxide particularly in batchwise dyeing. In printing and certain continuous dyeing processes sodium hydroxide enhances reduction potential but impairs the stability of the reducing agent, increasing the danger of premature loss of reducing action, particularly during the drying operation prior to steaming. In these processes carbonates give greater stability and hence are preferred [243]. There is little difference between sodium and potassium carbonates in terms of effect on the reducing agent, but there are advantages to be gained from using potassium carbonate to prepare relatively concentrated print pastes and pad liquors. Not only does potassium carbonate have a higher aqueous solubility at 20 °C (112% w/w) than sodium carbonate (21%), but the potassium leuco salts of vat dyes are also more soluble [29]. It is important to ensure the presence of excess alkali to counteract that consumed by the reducing agent and the substrate, as well as any reducing agent lost through atmospheric oxidation of the system [30].

Electrolyte may be used to enhance exhaustion of the leuco dye, particularly in batchwise dyeing. The use of electrolyte in the essentially 'short-liquor' printing and continuous dyeing processes is seldom necessary and could be inadvisable, as it may promote tailing during padding. However, electrolyte plays a positive part in those continuous processes in which a dispersion of the pigment form of the dye is applied first followed by separate application of reducing agent in the so-called chemical pad. The amounts of alkali and electrolyte

Table 12.37 Redox recipes used in indirect electrolysis application of indigo to cotton yarn [241]

Recipe	Components	Concentrations
1	Iron(III) chloride	0.18 mol/l
	Iron(II) chloride	0.06 mol/l
	Gluconic acid	0.30 mol/l
	Sodium heptagluconate	0.12 mol/l
	Calcium carbonate	0.09 mol/l
	Calcium chloride	0.09 mol/l
	Sodium hydroxide	to pH 11.5
2	Iron(III) sulphate hexahydrate	0.052 mol/l
	Iron(II) sulphate heptahydrate	0.060 mol/l
	Calcium heptagluconate	0.129 mol/l
	Anionic dispersing agent	0.5 g/l
	Sodium hydroxide	17.1 g/l pH 11.5
3	Iron(III) sulphate hexahydrate	61.3 g/l
	Triethanolamine	227 g/l
	Sodium gluconate	2 g/l
	Sodium hydroxide	69 g/l pH 13.5
4	Iron(III) chloride hexahydrate	54.0 g/l
	Sodium gluconate	54.5 g/l
	Calcium chloride	11.1 g/l
	Calcium heptagluconate	24.5 g/l
	Sodium hydroxide	20.0 g/l pH 11.4

Table 12.38 Summary of advantages and disadvantages of the three most important types of reducing agent for indigo, vat or sulphur dyeing [239]

Sodium dithionite	Advantages (1) sufficient reduction potential for vat, sulphur or indigo dyeing (2) good stability of leuco vat dyebaths Disadvantages (1) waste water loading; inhibits biological degradation and leads to a greater oxygen demand (2) can cause over-reduction at higher temperatures (3) special safe storage facility required
Sulphinic acid derivatives	Advantages (1) sufficient reduction potential for vat, sulphur or indigo dyeing (2) especially suitable for high-temperature dyeing methods (3) good resistance to oxidation by air Disadvantages (1) as for dithionite disadvantage (1) (2) potentially temperature-dependent
Hydroxyacetone	Advantages (1) biologically degradable (2) ease of dosing in liquid form (3) very good stability to storage Disadvantages (1) does not reach full reduction potential and thus mainly suitable for indigo and sulphur dyes (2) persistent odour (3) limited commercial production

obviously vary widely according to dyeing parameters (such as the liquor ratio) and the dyes used. A fully optimised computer-based program for recipe-specific calculation of quantities of sodium dithionite, sodium hydroxide and electrolyte has been published [244]. The advantage of such a program is that it enables exact quantities to be calculated, thus giving cost savings in chemicals and effluent treatment.

Levelling agents are frequently used, since the initial strike by leuco vat dyes can be rapid. A nonionic surfactant such as cetyl poly(oxyethylene) alcohol of optimum chain length (such as structure 12.25) is particularly useful because it can also act as a wetting agent. Poly(ethylene imine) derivatives of fatty alcohols behave in a similar way. On the other hand, certain products that act through a complexing mechanism are not surface-active; for example, one such proprietary product is based on poly(vinylpyrrolidone). Wetting and dispersing agents are also useful, particularly with inadequately prepared substrates.

Aliphatic sulphonates are widely used as wetting agents, particularly in combination with non-surfactant levelling agents. Any surfactants used must be stable under the alkaline reducing conditions. For continuous pad application they should also have a low propensity to foam; phosphoric esters are preferred to aliphatic sulphonates in this respect and in regard to the amount of pad liquor absorbed [221]. Dispersing agents, sometimes referred to as protective colloids, help to maintain the particulate distribution of the vat dye in pigment form and also inhibit aggregation of sparingly soluble leuco compounds; naphthalenesulphonic acid/formaldehyde condensates are especially useful. They are also essential additives in the application of vat dyes by the so-called pigmentation methods, using either the unreduced vat dyes themselves or, less frequently, acid leuco compounds [245].

A sequestering agent such as EDTA will prevent the formation of insoluble metal salts of vat leuco compounds. Trace metal ions would otherwise interfere with the application process and with level dyeing. It has been reported [246] that sequestering agents of the alkylphosphonate type can retard the uptake of vat dyes. An addition of pyrocatechol or tannic acid can help to counteract the well-known propensity of certain yellow and orange vat dyes to induce fibre tendering, whilst the addition of glucose or sodium nitrite can help to prevent the over-reduction of certain dyes.

Rinsing after exhaustion of the leuco vat dye has a marked influence on the final result, especially as regards the final hue, depth of shade and fastness properties. Figure 12.26 illustrates the effect of rinsing temperature and pH on the colour yield of dyeings of pyranthrone (12.59; CI Vat Orange 9). In general, yield decreases significantly with increasing temperature and to some extent with increasing pH, particularly at 70 °C. Dyeings tend to be duller after rinsing at a high temperature and alkaline pH, although this effect varies from dye to dye. Overall, rinsing should be carried out thoroughly at a low temperature and at pH 7 [247]. Rinsing should be neither too brief (inefficient) nor too prolonged (wasteful of water and processing time). A study of aftertreatments in jet and overflow machines [248] has shown advantages from optimising the rinsing process in relation to the concentrations of residual dithionite at the end of the dyeing stage and after rinsing. The dithionite is measured by titration, either manually by iodometry or automatically in an atmosphere of nitrogen according to the hexacyanoferrate method. A nominal target value (between 2 and 4 g/l) is set for the dithionite concentration at the end of dyeing, depending on dyeing machine type, fabric quality and dyes present. Starting from this value, a defined amount of rinsing water is used to dilute the dyebath in a given time, aiming for a final concentration of 0.5 g/l after rinsing. This procedure implies that complete removal of dithionite is unnecessary.

12.9.2 Oxidation

Various methods have been used for the reoxidation of vat leuco dyeings; atmospheric skying, hypochlorite, chlorite and acidified dichromate are now rarely employed. Atmospheric oxidation can be difficult to control and thus uneven; with some dyes it is also too slow, particularly for continuous methods. Sodium hypochlorite is used only for those few black dyes that tend to become dark green when oxidised with peroxide; obviously hypochlorite should be avoided with the many chlorine-sensitive dyes. Similarly sodium chlorite, acidified to below pH 5 with acetic acid, can only be used with certain dyes, although with these it certainly gives rapid oxidation. Dye selectivity is also a drawback with

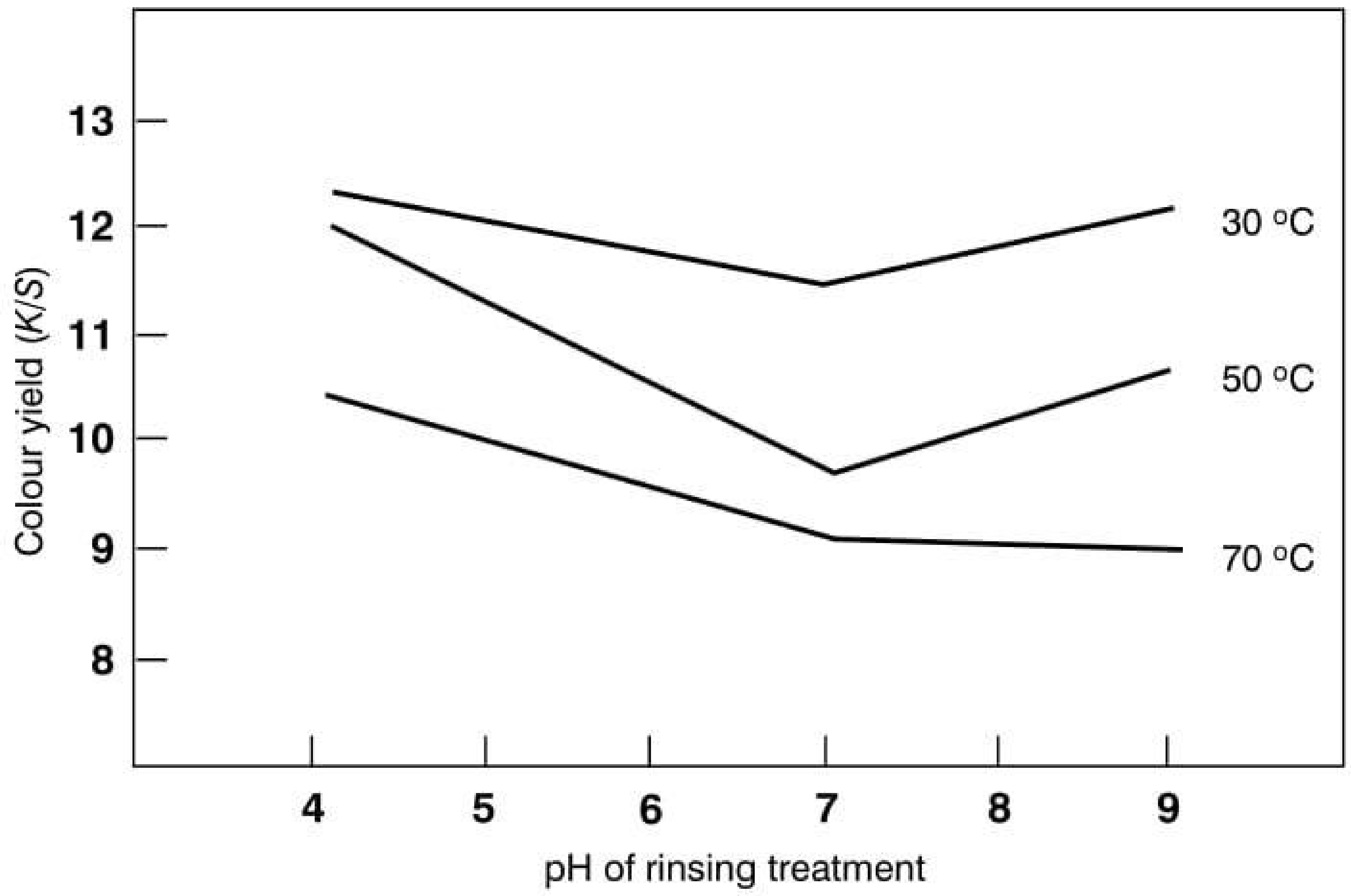
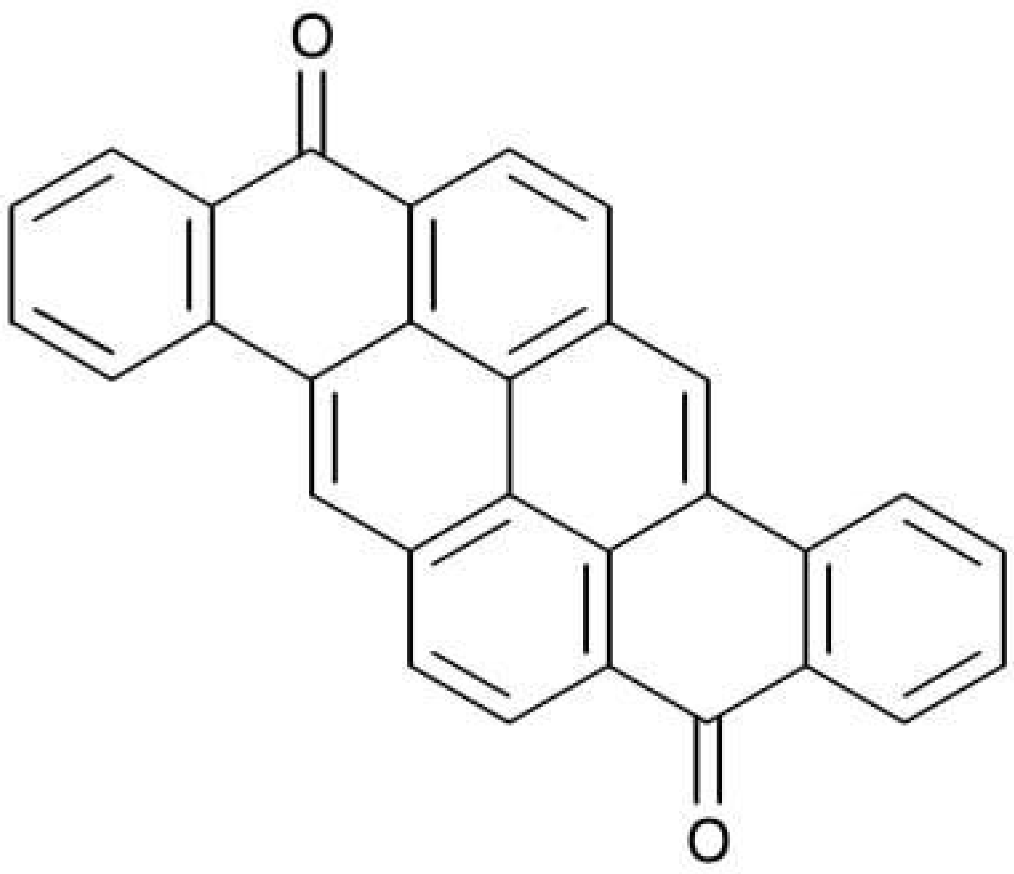


Figure 12.26 Effect of temperature and pH of rinsing on the colour yield of dyeings of CI Vat Orange 9 [247]



12.59
Pyranthrone

acidified dichromate, since not surprisingly its chelating potential can give rise to hue variation, especially with sensitive blues and greens. The AOX-generating potential of the chlorine-containing oxidants and the toxicity of chromium also make these compounds environmentally undesirable. The most commonly used oxidising agents are hydrogen peroxide, sodium perborate and sodium *m*-nitrobenzenesulphonate [30]. Sodium nitrite acidified with sulphuric acid is used to hydrolyse and reoxidise the solubilised vat leuco ester dyes.

Hydrogen peroxide and sodium perborate remain the mainstay of the vat dye reoxidation process; the amounts to be used vary widely according to the conditions of processing. Consequently, dye manufacturers' recommendations can only be used as guidelines and may need modification according to the machinery and conditions used. Many important factors have to be considered, especially the liquor ratio, the contact frequency between liquor and goods, the particular dyes and the depth of shade, as well as the efficiency with which the reduction liquor has been rinsed out. For example, in a long-liquor (20:1 to 30:1) winch dyeing process as little as 0.5–1.0 g/l hydrogen peroxide (130 vol.) or sodium perborate at 50 °C is usually adequate; this may be increased to 3–5 g/l at 50–60 °C in short-liquor jig dyeing. The rate of oxidation can be controlled by addition of acetic acid to neutralise excess alkali carried over from reduction but care should be taken not to over-acidify as this would tend to convert the sodium leuco compound into the less soluble acid leuco form. Some blues are exceptionally sensitive to alkaline oxidation, however, and must therefore be rinsed thoroughly before oxidation in the presence of a small amount of acetic acid. Over-oxidation can often be corrected by again reducing the dyeing and then reoxidising under more carefully controlled conditions.

Sodium *m*-nitrobenzenesulphonate has been proposed as an oxidising agent for vat dyes. It is available as a proprietary product and is claimed to react with leuco compounds more quickly than does peroxide. The solubilised vat leuco esters are most commonly hydrolysed and reoxidised to the insoluble parent dye using sodium nitrite and sulphuric acid. Alternative oxidising agents for vat leuco esters include hydrogen peroxide and ammonium metavanadate (NH_4VO_3), persulphates and nitric acid [218].

12.9.3 Soaping

The final soaping at the boil of reoxidised vat dyeings must be regarded as an integral part of the application sequence, rather than an optional extra, since it determines the reproducibility of colour and fastness. The traditional process was to use a boiling bath containing 3–5 g/l Marseilles (olive oil) soap and 2 g/l sodium carbonate, usually for 10–15 minutes in a batchwise process. Soaping times of less than a minute are the norm in continuous pad–steam ranges, however, and it is then preferable to select dyes that show only a slight change in colour during soaping [30,245]. Synthetic surfactants, particularly of the nonionic type, are now used instead of soap, although they contribute to an increased effluent load and should be used sparingly [247]. Boiling off in water alone is preferable as the dyeings obtained are similar and in no case do they exhibit fastness ratings inferior to those from washing with a detergent. This is clearly an important finding in view of the fact that vat dyeing effluent is already heavily contaminated [247].

Various mechanisms have been proposed to explain what happens during soaping. Investigations [249,250] suggest that dye molecules at first aligned along the fibre axis are converted by soaping to crystalline aggregates reoriented at right angles to the fibre axis. Evidence exists, however, to show that some dyes are present as amorphous aggregates both before and after soaping, whereas reoxidised indigo particles are crystalline even before soaping. Another possibility is that an initially metastable crystal modification of the dye is converted by soaping into a more stable crystalline form.

12.9.4 Continuous dyeing and printing

In general, the reducing, oxidising and soaping agents for continuous dyeing are the same as those used in batchwise dyeing, although they have to be used at higher concentrations. In some cases there may be a preference for more stable reducing agents than dithionite, such as sulphoxylates; in continuous dyeing dithionite is still the most widely applicable product [221], although sulphoxylates are undoubtedly preferred in printing. In continuous pigment padding a migration inhibitor is essential to prevent tailing, twosidedness or general unlevelness, as well as to stabilise the pad liquor against pigment sedimentation [221]. It is important to select agents that promote the tendency of dye particles to agglomerate, as this is the mechanism whereby migration is inhibited. Poly(acrylic acid) derivatives, alginates, branched polysaccharides and block copolymers of ethylene oxide and propylene oxide have proved useful. Conversely, some printing thickeners such as locust bean gum, starch ethers, guar derivatives and carboxymethylcellulose have been less successful in preventing particulate migration in continuous dyeing, thus indicating that a mere increase in viscosity is ineffective in controlling migration [221].

In direct printing by an all-in, single-stage process the most favoured reducing system is sodium formaldehyde-sulphoxylate with potassium carbonate as alkali. A thickening agent is required; British gum thickening may accelerate decomposition of the reducing agent but otherwise the choice of thickening agent is not critical. A hydrotrope helps to improve fixation in steam. A typical print paste recipe is given in Table 12.39. A reduction accelerator such as an aminoanthraquinonesulphonic acid may be added. The flash-ageing method is a two-stage process in which the initial print paste contains dye and thickener only [251]. The reducing agent and alkali are subsequently applied by padding. In this process exposure to air prior to steaming is minimal and the less stable sodium dithionite can be used as the reducing agent. The thickening agent should coagulate in the presence of alkali in order to inhibit bleeding of colour; alternatively a gelling effect can be obtained by adding a borate to a thickener such as locust bean gum, as described in section 10.8.1. Mixtures of thickeners are often formulated to attain the required degree of coagulation; if this is exceeded there can be problems at the washing-off stage.

Table 12.39 Typical print paste recipe for a single-stage process with vat dyes

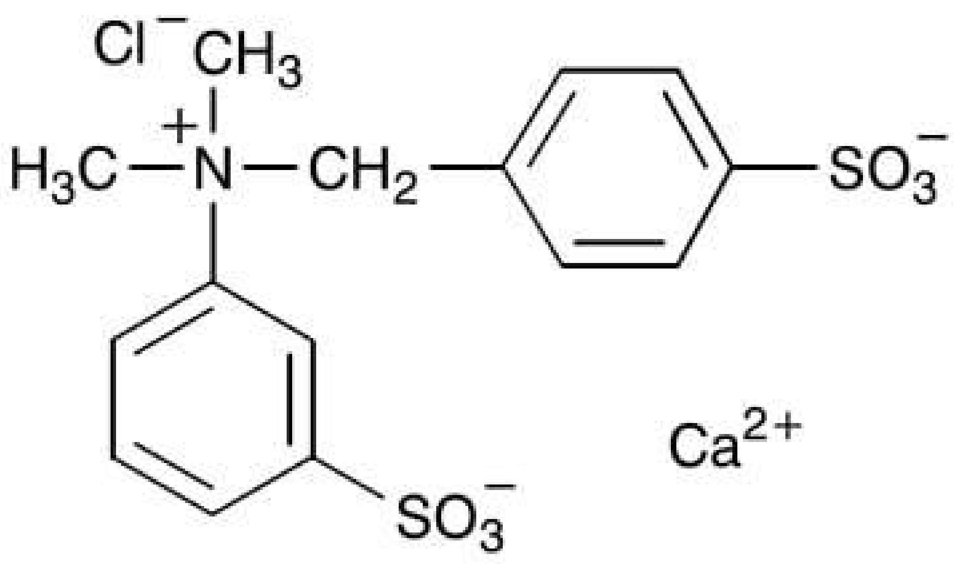
	Amount (% w/w)
Vat dye	x
Potassium carbonate	15
Sodium formaldehyde-sulphoxylate	8
Glycerol (hydrotrope)	5
Thickening agent	24
Water to	100

The solubilised vat leuco esters are particularly suitable for printing. There are two main methods of hydrolysis and reoxidation. In the first sodium nitrite is incorporated in the print paste and this is converted to nitrous acid by a short immersion of the printed goods in dilute sulphuric acid after drying and steaming. Sodium chlorate is used in the second method by incorporation into the print paste together with ammonia (to maintain alkalinity in the paste) and a steam-activated acid generator such as ammonium thiocyanate (NH_4SCN); an oxidation catalyst, ammonium metavanadate (NH_4VO_3), is also used.

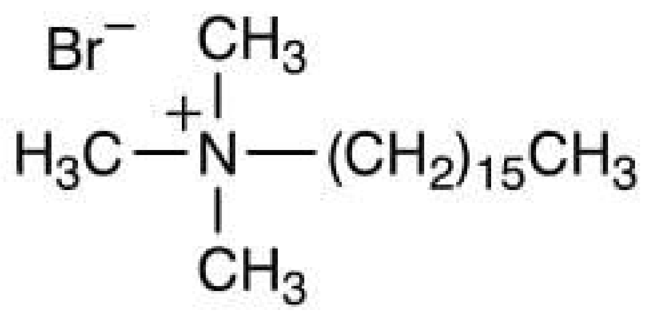
Vat dyes can be used as illuminant colours in discharge styles where the discharged grounds may be azoic, direct or reactive dyeings. In such cases the quantity of reducing agent has to be increased since it is needed for discharging the other dyes as well as for reducing (but not discharging) the vat dyes. A further agent, known as a leucotrope, may also be needed if white discharges are required; leucotropes act as discharge (or stripping) promoters and are described below.

12.9.5 Correction of faults

Levelling and partial stripping may be carried out in a reducing bath using sodium dithionite and sodium hydroxide in combination with a suitable levelling agent such as those described earlier. Greater quantities of levelling agent can be employed to increase the stripping effect. The complexing agents are more effective than nonionic levelling agents. Certain quaternary ammonium compounds (such as structures 12.60 and 12.61) promote stripping by complexing with the leuco form of the dye. These products, often referred to as leucotropes, are used in conjunction with sodium dithionite and sodium hydroxide to give an effective stripping action.

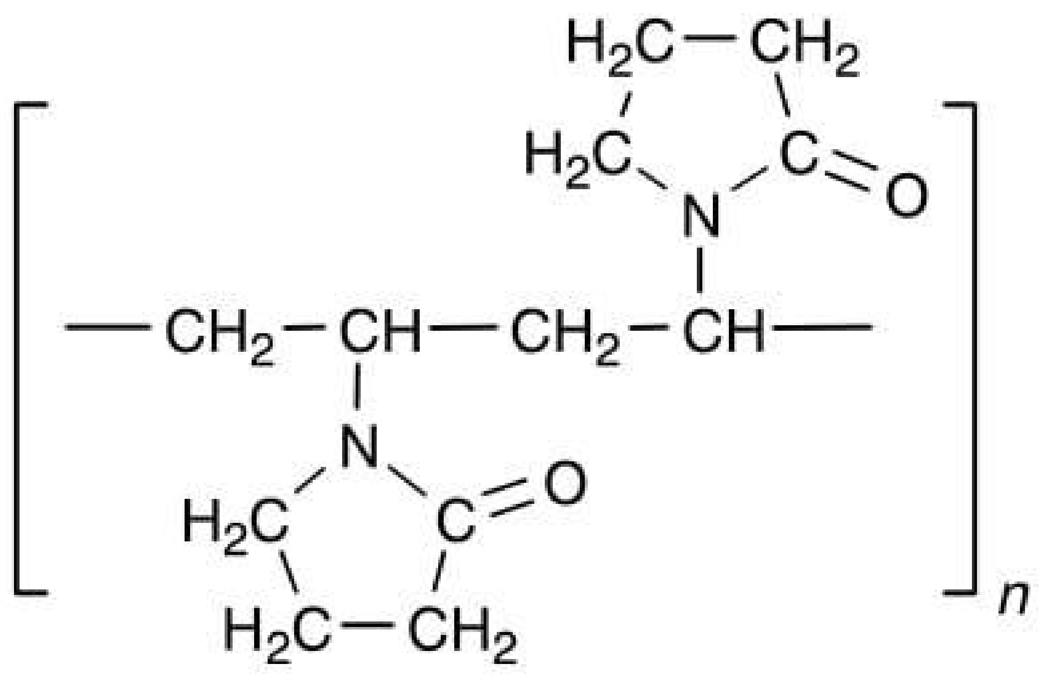


12.60



$\mathrm{Br^-}\ \mathrm{H_3C-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-(CH_2)_{15}CH_3}$

12.61



12.62

Poly(vinylpyrrolidone) (12.62) has an M_r range of 1–9 × 10^4 and a DP of 100–800. The macromolecular chains are considerably folded in aqueous solution. The pyrrolidone rings are oriented at right angles to the carbon chain, giving a hydrophilic series of keto groups on one side and hydrophobic propylene segments on the other [252]. This polymer readily forms complexes with vat leuco anions in alkaline dithionite solution to give a highly effective stripping action.

12.9.6 Ecological considerations

Several ecological points have been mentioned above; an overall summary [220,253] will be useful here. Certain factors in dealing with ecological problems in dyehouses are common to all textile dyes, not just vat dyes. The primary approach, of course, is precise optimisation of all parameters so that the minimal quantity of all additives is used, thus ensuring minimum loading of the waste water. Dyeing at as low a liquor ratio as possible saves water and energy, as well as giving a lower volume of effluent. Shorter liquors give more concentrated waste water but this need not be a disadvantage, since it may facilitate subsequent treatments including precipitation, flocculation, filtration or centrifugation. The second factor is to choose products, both colorants and auxiliaries, that are the most environmentally favourable on the market; all reputable manufacturers and suppliers are working diligently in this direction. Indeed, the chemical industry and the textile wet processing sector have shown a responsible and increasingly effective approach to the varied and often difficult environmental problems that have arisen.

As already noted, vat dyeings generally give more heavily loaded waste waters than direct or reactive dyeings but these loads are reasonably treatable. A specific advantage of vat

Table 12.40 An environmental assessment of commercial brands of vat dyes [253]

Eliminability of organic halogen compounds	Completely eliminated by adsorption onto sewage sludge; no organic halogen compounds in the outlet of the treatment plant
Ecotoxicity	Insoluble in water, therefore not toxic to bacteria, algae or fish; not bioavailable, so do not accumulate in living organisms
Heavy metal impurities	Range-specific differences
Dispersants and additives	Range-specific differences

Table 12.41 Environmental properties of reducing agents for dyeing with vat dyes [253]

Inorganic	Sodium dithionite	Advantages (1) Universal and highly effective (2) Free from heavy metals Disadvantage Sulphite/sulphate in waste water (oxygen-consuming, may damage piping)
Organic	Hydroxyacetone (other products with improved properties being developed)	Advantages (1) Free from sulphite and heavy metals (2) Nontoxic to aquatic life (3) Readily biodegradable Disadvantages (1) Increased TOC/COD (2) Weaker reductive effect than dithionite

Table 12.42 Remedial action for operating with reducing agents for vat dyes [253]

Reducing agents	Recommendations for dealing with the drawbacks
(1) Dithionite and derivatives	Minimising the concentration by optimising Oxidation of sulphite to sulphate (isothermal dyeing with oxidation in the dyebath for pale shades)
(2) Hydroxyacetone	In certain applications dithionite can be replaced by hydroxyacetone (e.g. indigo dyeing)
(3) Mixtures of dithionite and hydroxyacetone	Used in optimum proportions for the particular application, it is possible to reduce contamination of the effluent by sulphite to the minimum

dyeing is that these insoluble dyes pose few hazards. The LD_{50} of vat dyes, determined by oral feeding to rats, exceeds 2000 mg/kg and they are non-toxic to fish. As yet, only one vat dye (CI Vat Green 9) has given a positive Ames test response and only one other (CI Vat Yellow 4) has given positive results for carcinogenicity [220].

Vat dyes exhibit another important advantage compared with direct and reactive dyes: their exceptionally high exhaustion leads to very little residual dye in the effluent. Furthermore, any dye that does enter the effluent is insoluble and can easily be removed by flocculation or precipitation; it is also readily adsorbed by sludge in biological treatment. Thus vat dyes that contain halogen pose no serious threat in the waste water [253]. Consequently the major contribution of vat dyes to effluent pollution arises from their content of dispersing agent, which may vary from one manufacturer to another. The difference between powder and liquid brands is pertinent here. Powder dyes, for example, can give a COD value of about 1500 mg/g, of which only 40% is from the dye and 60% from the dispersing agent. For liquid dyes the corresponding value is 600 mg/g, of which 50% is from the dye and only 25% from the dispersing agent and hydrotrope; the hydrotrope is readily biodegradable [220]. Thus, as far as the dyes themselves are concerned, the situation is summarised in Table 12.40. There are, of course, important contributions to effluent pollution from levelling agents, sequestrants, antifoams, migration inhibitors or thickening agents applied in conjunction with these dyes.

Since the almost universal reducing agent is sodium dithionite, there is a serious problem of sulphite and sulphate ions in the effluent, the sulphite usually being mostly oxidised to sulphate. Directly added electrolyte may be present but this is usually less important than with direct or reactive dyes. Hydroxyacetone has the advantage of biodegradability, although it contributes to the organic carbon content. As already mentioned, there are environmental benefits to be gained from using mixtures of sodium dithionite and hydroxyacetone [253]. The overall situation with regard to reducing agents is summarised in Tables 12.41 and 12.42.

The oxidation process using hydrogen peroxide poses no serious environmental problem. As indicated in section 12.9.3, there are obvious advantages to be gained from a purely aqueous boil rather than soaping with a surfactant. By employing an optimised isothermal dyeing process including metering of the dyes, reoxidation can be carried out in the exhaust dyebath giving savings in water, time and energy, as well as ensuring that all sulphite from the dithionite is oxidised to sulphate before discharge to effluent [253].

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